PB-237 366

REDUCTION OF ATMOSPHERIC POLLUTION

G. J. Vogel, et al

Argonne National Laboratory

Prepared for:

National Environmental Research
Center

June 1974

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-650/2-74-057	2.	3. PB 237 366
4. TITLE AND SUBTITLE Reduction of Atmospheric Pollution by the Application of Fluidized-Bed Combustion		5. REPORT DATE June 1974
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) G. J. Vogel, M. Haas, W. Swift, J. Riha, C. B. Schoffstoll, J. Hepperly, and A. A. Jonke		8. PERFORMING ORGANIZATION REPORT NO. ANL/ES-CEN-1006
9. PERFORMING ORGANIZATION NAME AND ADDRESS Argonne National Laboratory 9700 South Cass Avenue Argonne, Illinois 60439		10. PROGRAM ELEMENT NO. 1AB013; ROAP 21ADB-011
		11. CONTRACT/GRANT NO. EPA-IAG-0199(D)
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development NERC-RTP, Control Systems Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Annual; 7/72-6/73
		14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT

The report gives results of a bench-scale and laboratory-scale experimental investigation of the feasibility of applying fluidized-bed combustion (FBC) of coal to power generation. The FBC concept would combust coal at elevated pressure (to 10 atm) in a fluidized bed of dolomite, which reacts with the SO2 formed during combustion. The partially sulfated dolomite is then regenerated using one of the two alternative techniques: a one-step reductive decomposition technique (converting CaSO4 to CaO and SO2); or a two-step technique involving the reduction of CaSO4 to CaS, followed by reaction of the CaS with H2O and CO2 to form CaCO3 and H2S. Results of the pressurized FBC tests indicate favorable air pollutant emission control, with 90-95% reduction in SO2 emission, and with NO levels of about 150 ppm, well below EPA's New Source Performance Standards for large coal boilers. Initial sorbent regeneration studies showed significant deactivation and decrepitation of the dolomite; further investigation is necessary in the area of regeneration.

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution	Electric Power Generation	Air Pollution Control	13B
Fluidized-Bed Processing	Regeneration (Engineering)	Stationary Sources	10A
Coal	Sulfur Dioxide	Pressurized Fluidized-Bed Combustion	13H, 07A
Combustion	Nitrogen Oxide (NO)		21D, 08G
Dolomite (Mineral)			21B, 07B

18. DISTRIBUTION STATEMENT Unlimited	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 133
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE 5.75

EPA Form 2220-1 (9-73)

.1.

EPA-650/2-74-057

REDUCTION OF ATMOSPHERIC POLLUTION BY THE APPLICATION OF FLUIDIZED-BED COMBUSTION

by

G. J. Vogel, M. Haas, W. Swift,
J. Riha, C. B. Schoffstoll, J. Hepperly, and A. A. Jonke

Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

Interagency Agreement No. EPA-IAG-0199(D)
ROAP No. 21ADB-011
Program Element No. 1AB013

EPA Project Officer: D. B. Henschel

Control Systems Laboratory
National Environmental Research Center
Research Triangle Park, North Carolina 27711

Prepared for

OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

June 1974

This report has been reviewed by the Environmental Protection Agency and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

TABLE OF CONTENTS

Page

ABSTRACT 9

I. SUMMARY. 10

II. INTRODUCTION 22

III. BENCH-SCALE, FLUIDIZED-BED, COMBUSTION-REGENERATION STUDIES. 23

A. Materials. 23

1. Coal 23
2. Additive 24
3. Kerosene 25

B. Equipment. 25

1. Pressurized, Fluidized-Bed Combustor 25
2. Fluidizing-Gas Supply System and 6-in.-dia Preheater 30
3. Fluidized-Bed Regenerator System 30
4. Analytical Equipment 33

C. Coal Combustion Experiments. 36

1. Comparison of SO_2 Retention in Old and New Combustion Units 36
2. High-Pressure Operation. 38

D. Regeneration of $CaSO_4$. 41

1. Two-Step Regeneration Experiments. 43
2. One-Step Regeneration of $CaSO_4$, Batch Operation. . . 47
3. One-Step Regeneration of $CaSO_4$, Continuous Operation. 53
4. One-Step Regeneration of Sulfated Dolomite, Continuous Operation 56
5. Regeneration by the Reaction, $CaSO_4 + CO \rightarrow CaCO_3 + SO_2$. 59
6. Kerosene Combustion Products 62

IV. LABORATORY-SCALE REGENERATION STUDIES. 63

A. Introduction and Review of Previous Work 63

B. Equipment. 64

C. Materials. 64

D. Results and Discussion 64

1. Two-Step Process 64
2. One-Step Reductive Decomposition Process, Low Temperature Studies. 86

TABLE OF CONTENTS (Cont'd.)

Page

3. Reaction of $CaSO_4$ and CO_2/H_2 at Temperatures of 1400°F and Less. 88
4. Removal of H_2S from Off-Gas by Reaction with Potassium Permanganate 90

V. TRACE-ELEMENT DISTRIBUTION STUDIES 91

A. Introduction 91

B. Applicability of Selected Methods for Analyzing Trace Elements of Interest 91

1. Analysis of Coal, Limestone, and Coal Combustion Residues by X-ray Spectrometric Analysis 93
2. Application of Nondispersive X-ray (NDXR) Spectrometry to Coal and Coal Combustion Residues 94

C. Flue-Gas Sampling. 94

1. Description of Sampling Location 96
2. Particulate Sampling 97
3. Treatment of Particulate Samples 100
4. Determination of Mercury in Particulate and Gaseous Emissions. 101
5. Determination of Inorganic Fluorides in Gaseous and Particulate Emissions. 102

VI. ACKNOWLEDGMENTS. 103

VII. REFERENCES 104

APPENDIX A. English to Metric Unit Equivalents 105

APPENDIX B. Specific Analytical Procedures for Solids Samples from Combustion and Regeneration Experiments 107

APPENDIX C. Operating Data and Results Obtained in Batch Regeneration Experiments in the 1- and 2-inch-Diameter Reactor 109

APPENDIX D. Thermodynamic Considerations Relating to the Conversion of Calcium Sulfate to Calcium Carbonate. 127

LIST OF FIGURES

No.	Title	Page
1.	Pressurized Combustion-Regeneration Equipment Schematic . .	26
2.	Six-in.-Dia, Pressurized, Fluidized-Bed Combustor	27
3.	Lower Section of Combustor	28
4.	Additive Hopper, Feeder, and Weigh Scale	29
5.	Six-in.-Dia, Fluidizing-Gas Preheater	31
6.	Three-in.-Dia, Fluidized-Bed Regenerator	32
7.	Combustion and Regeneration Pilot Plants	34
8.	Gas Sampling and Analysis System	35
9.	Comparison of Sulfur Retention in Atmospheric Combustion Experiments Conducted in Old Atmospheric and New Pressurized Combustors	40
10.	Conditions and Results for Experiment REDUC-8	51
11.	Conditions and Results for Experiment REDUC-9	52
12.	Kerosene Input and CH_4 Concentration in Process Off-Gas for Experiment REDUC-10	54
13.	Conditions and Results for Experiment REDUC-10	55
14.	Sulfur Distribution in Regeneration Experiment REDUC-12 . .	58
15.	Two-in.-Dia, Fluidized-Bed Reactor System	65
16.	H_2S Concentration in Effluent-Gas Stream during Regeneration Step of Experiment CATS-22	67
17.	H_2S Concentration in Effluent-Gas Stream during Regeneration Step of Experiment CATS-23	69
18.	H_2S Concentration in Effluent-Gas Stream during Regeneration Step of Experiment CATS-24	71
19.	H_2S Concentration in Effluent-Gas Stream during Regeneration Step of Experiment CATS-26	72

LIST OF FIGURES (Cont'd.)

No. Title Page

20. Conceptual Two-Stage, Fluidized-Bed, Regeneration Reactor. 76

21. Infrared Spectrum of Material Taken from Cycle Two of the Cyclic Sulfation-Regeneration Experiment: A. Material from Sulfation Step; B. Material from Reduction Step; C. Material from Regeneration Step 79

22. Infrared Spectrum of Material Taken from Cycle Two of Experiment CATS-22: A. Material after Reaction with H_2S; B. Material from Regeneration Step 80

23. Electron Microprobe Scan of Particles Taken from the Second-Cycle Sulfation Step of the Sulfation-Regeneration Experiment 81

24. Electron Microprobe Scan of Particles Taken from the Second-Cycle Reduction Step of the Sulfation-Regeneration Experiment 82

25. Electron Microprobe Scan of Particles Taken from the Second-Cycle Regeneration Step of the Sulfation-Regeneration Experiment 83

26. Equilibrium Concentrations of SO_2 for the Reaction $CaSO_4 + CO \rightarrow CaCO_3 + SO_2$ 87

27. Experimental Flow System for Flue-Gas Sampling 96

28. Apparatus for Particulate Sampling of Flue Gas 98

29. Single Impactor Stage 99

30. Design of Impactor Collection Cups 99

31. Apparatus for the Determination of Particulate and Gaseous Emissions of Mercury in Flue Gas 102

LIST OF TABLES

No. Title Page

1. Chemical Characteristics of Coal. 23
2. Size Distribution of Coals. 24
3. Chemical Composition of Additives 24
4. Size Distribution of As-Used Additives. 25
5. Chemical and Physical Characteristics of ANL Kerosene . . . 25
6. Flue-Gas Analytical Equipment 37
7. Operating Conditions and Results for Experiment SD-11 . . . 39
8. Particle-Size Distribution of Feed and Product Materials for Experiment ARK-3. 41
9. Operating Conditions and Results for Experiment ARK-3 . . . 42

10a. Summary of Operating Conditions, Bench-Scale, Batch Regeneration Experiments, Two-Step Process. 45

10b. Summary of Operating Conditions and Results, Bench-Scale, Batch Regeneration Experiments, Two-Step Process. 46

11a. Summary of Operating Conditions, Bench-Scale, Regeneration Experiments, One-Step Process 49

11b. Summary of Operating Conditions and Results, Bench-Scale Regeneration Experiments, One-Step Process. 50

12. Sulfur Balance for Experiment REDUC-10. 56
13. Comparative Particle-Size Distributions of Materials Fed and Removed from Experiment REDUC-12. 59
14. Chemical Composition of Solids in Exp. REDUC-12 59
15. Operating Conditions and Results for Experiment REDUC-13. . 61
16. Conditions and Results for H_2S Addition and Regeneration Steps of Experiment CATS-22 66
17. Screen Analysis of Initial and Final Bed Material and Fines for Experiment CATS-22. 68

LIST OF TABLES (Cont'd.)

No.	Title	Page
18.	Conditions and Results for H_2S Addition and Regeneration Steps of Experiment CATS-23	68
19.	Conditions and Results for H_2S Addition and Regeneration Steps of Experiment CATS-24	70
20.	Conditions and Results for H_2S Addition and Regeneration Steps of Experiment CATS-26	72
21.	Process Conditions and Bed Compositions for Experiment CATS-28	73
22.	Composition of Effluent Gas Stream during Reaction of $CaSO_4$ with CO/CO_2 (Reduction Step) in Experiment CATS-27. .	77
23.	Summary of X-ray Analyses of Particles from Fluidized-Bed Experiments	84
24.	Reaction Conditions and Analytical Results for Studies on $CaSO_4$-H_2-CO_2 Reaction	89
25.	Applicability of Selected Analytical Methods for Trace Elements in Coal Combustion	92
26.	Analysis of Coal and Coal Combustion Products with Non-dispersive X-ray Spectrometer	95
27.	Dimensions of Cascade Impactor Jets	100

REDUCTION OF ATMOSPHERIC POLLUTION BY THE APPLICATION OF FLUIDIZED-BED COMBUSTION

Annual Report
July 1972 - June 1973

by

G. J. Vogel, M. Haas, W. Swift, J. Riha,
C. B. Schoffstoll, J. Hepperly, and A. A. Jonke

ABSTRACT

The Argonne National Laboratory (ANL) program for demonstrating the feasibility of fluidized-bed combustion for possible use in power and steam plant applications is divided into three studies: a) combustion of fossil fuels in a pressurized combustor, b) regeneration of sulfated additive for reuse in the combustor, and c) evaluation of the type and level of trace-element pollutants in the flue gas.

A fluidized-bed combustion pilot plant and a fluidized-bed regenerator, both capable of operating at 10-atm pressure, have been tested and operated. In combustion of coal at 9-atm pressure and 1550°F (843°C)*, high (>90%) retention of sulfur in the fluidized bed of dolomite has been obtained with continuous addition of fresh dolomite at a Ca/S ratio of 3. The NO level in the flue gas has been low, <150 ppm. Two favored methods for regenerating the sulfated dolomite have been studied: a one-step reductive decomposition of the $CaSO_4$ to CaO at ∿1950°F to release SO_2, and a two-step process consisting of reduction of $CaSO_4$ to CaS at ∿1700°F followed by reaction of CaS with H_2O/CO_2 to release H_2S. In results to date, complete release of sulfur from the particles has not been achieved by either regeneration method, and decrepitation of the particles has been observed. Equipment has been constructed and analytical methods have been selected for determining the quantity and concentration of trace element pollutants in solid or gaseous form in the flue gas.

---

*Table of English to metric unit equivalents presented in Appendix A.

I. SUMMARY

Argonne National Laboratory is investigating pollution control aspects of pressurized, fluidized-bed combustion in a program funded by the Control Systems Laboratory of the Environmental Protection Agency. The program consists of investigating (1) the effects of operating variables in reducing pollutant emissions when fossil fuels are combusted in a pressurized, fluidized bed of sulfur-acceptor additive, (2) the regeneration of this additive for reuse and the recovery of the sulfur, and (3) the quantity and type of trace-element pollutants in the flue gas.

In these studies, coal is completely combusted in a fluidized bed of dolomite using an excess of oxygen. When sulfur contained in the coal is released during combustion in the oxygen-excess environment, $CaSO_4$ is formed by reaction of the SO_2 with the calcium. For regenerating $CaSO_4$, emphasis is being placed on two regeneration methods. One is reductive decomposition of $CaSO_4$ to CaO and SO_2 at ~2000°F:

$$CaSO_4 + CO \text{ (or other reductant)} \rightarrow CaO + SO_2 + CO_2$$

A relatively concentrated stream of SO_2 is produced, which can be processed in a sulfur recovery plant. The other method is a two-step process in which $CaSO_4$ is reduced to CaS at ~1600°F and then the CaS is reacted with CO_2/H_2O at ~1100°F to release H_2S for sulfur recovery:

$$CaSO_4 + 4CO \text{ (or other reductant)} \rightarrow CaS + 4CO_2$$

$$CaS + H_2O + CO_2 \rightarrow H_2S + CaCO_3$$

Bench-Scale, Fluidized-Bed, Combustion-Regeneration Studies

Materials. The coal used in the combustion experiments was a bituminous coal from one of two sources: a Pittsburgh seam coal from Consolidation Coal Co.'s Arkwright mine and an Illinois coal from Peabody Coal Co.'s Christian County Mine. Coal was ground to -14 mesh before use.

Two additives used in the studies were Tymochtee dolomite from Ohio and No. 1359 limestone from Virginia. Additives were double screened, using 14- and 100-mesh screens.

Kerosene and cylinder gases were obtained from ANL stock.

Equipment. The ANL bench-scale equipment, designed for operation to 10 atm, consists of a fluidized-bed combustor and an additive regeneration reactor that have a common off-gas system (cyclones, filters, gas-sampling equipment, pressure letdown valve, and scrubber). The experimental system is thoroughly instrumented and equipped with an automatic data-logging system.

The combustion unit consists of a 6-in.-dia pipe, 11 feet long. The exterior of the pipe is wrapped with electrical heaters (to heat the bed from room temperature to the coal-ignition temperature at the start of an experiment) and cooling coils (to cool the bed during coal combustion). Additional cooling is provided by hairpin coils immersed in the fluidized bed. Coal and additive are conveyed pneumatically and continuously to the fluidized bed from weighed hoppers. Each hopper has a rotary valve at the bottom for metering the coal or additive to the air-conveying stream. A constant bed level is maintained in the combustor by use of an internal overflow pipe.

The 3-in.-dia regenerator was fabricated by casting a 2-1/2-in. layer of refractory in an 8-in.-dia pipe. This assembly was enclosed in a 12-in.-dia pressure shell. Cooling and heating coils extend along the length of the 8-in.-dia pipe. As in the combustor, solids are conveyed pneumatically to the fluidized bed and bed solids are removed by use of an internal overflow pipe.

Coal Combustion Experiments. Construction of the 6-in.-dia bench-scale equipment for fluidized-bed combustion was completed, and operational testing of the plant was started at 1-atm pressure. At this pressure, the data obtained on SO_2 retention and NO levels were compared with those obtained in the previously installed atmospheric-pressure combustor. The intent was to determine whether design differences in the combustion zone would result in marked differences in the SO_2 and NO levels in the flue gas. The principal design differences are the following: (1) the presently installed combustor has cooling tubes in the combustion zone whereas the previous one did not, (2) coal and additive are injected vertically into the bed (rather than horizontally, as in the previously installed unit), and (3) bed material is removed continuously rather than batchwise.

During the atmospheric-pressure experiment with the new combustor, Illinois coal and limestone No. 1359 were fed continuously to the combustor. The operating conditions were a bed temperature of 1470°F, a Ca/S (calcium in the dolomite feed to sulfur in the coal feed) mole ratio of 3.5, a superficial gas velocity of 2.8 ft/sec, and 2.7 vol % O_2 in the flue gas. Under these conditions, the flue-gas SO_2 level was 420 ppm, corresponding to the retention of 89% of the sulfur by the bed. This retention is similar to that obtained in the previously installed combustor operated at the same conditions. The flue-gas NO level of 375 ppm was within the range expected for fluidized-bed coal-combustion experiments. Thus it was concluded that design differences in the two combustors did not markedly affect the SO_2 and NO levels.

In subsequent experiments, system pressures were increased gradually until the combustor was operating at design pressure. Excellent sulfur retention (95%) in the bed and low levels of NO (150-200 ppm) in the flue gas were demonstrated at 9-atm pressure. In these experiments, Tymochtee dolomite and coal were fed continuously to give a Ca/S mole ratio of three. Gas velocity through the bed was 2.5 ft/sec and the bed temperature was 1515°F.

Regeneration of $CaSO_4$. During the past year, several regeneration experiments were made using the newly completed 3-in.-dia regeneration unit. Information regarding the operation of the unit and the potential of the one- and two-step regeneration processes was obtained.

The two-step regeneration process involves the reduction of calcium sulfate to calcium sulfide with carbon monoxide in the first step, then reacting the calcium sulfide with carbon dioxide and steam to form $CaCO_3$ in the second step. Both steps were investigated in the 3-in.-dia, bench-scale regenerator. Four reduction experiments (RED-1, -2, -3, and -4) were performed, and with the exception of the first reduction experiment (RED-1), each was followed by a CO_2/steam regeneration experiment (REGEN-2, -3, and -4).

In a reduction run, 2.4 or 3.5 kg of calcium sulfate (Drierite) was charged to the regenerator; the height of the settled bed was 2 and 3 feet, respectively. The bed was maintained at an operating temperature of ∿1700°F by burning the carbon monoxide with oxygen. Enough excess CO was fed to allow for the reduction of the calcium sulfate. The pressure in the regenerator, initially near atmospheric, was then increased to the operating pressure.

A regeneration run was begun immediately following each reduction run without shutting down the equipment. To start the regeneration, the temperature of the bed was dropped to ∿1100°F from the reduction process temperature of 1700°F. Carbon dioxide, diluted with nitrogen, was passed through the bed and then steam was added to this mixture.

Experiments were conducted at pressures of 8, 30, 75, and 135 psig in this equipment-testing phase of the investigation.

Samples were taken of the final bed after the two steps (one step only in the first experiment) had been completed and were analyzed for sulfide and total sulfur content. In the first experiment, no sulfide (<0.3%) was found in the sample which contained 18.0% total sulfur. The absence of reduction may have been caused by an oxygen concentration in the bed that was too high. In RED-2 and RED-3, oxygen concentration was carefully controlled (oxygen concentration in the exit gas was kept at a minimum), and sulfide was formed in the bed. After the regeneration step in RED-REGEN-2, 37% of the sulfur was present as sulfide (S_{total} = 20.2%; $S^{=}$ = 7.5%) and in RED-REGEN-3, 44% (S_{total} = 26.2% and $S^{=}$ = 11.6%).

If it is assumed that the sample of bed removed after the regeneration step contained only (1) unreacted $CaSO_4$, (2) CaS made in the reduction step but not converted to $CaSO_4$ by steam/CO_2, and (3) $CaCO_3$ from the steam/CO_2 reaction with CaS, the final bed of RED-REGEN-2 contained 54% $CaSO_4$, 17% CaS, and 29% $CaCO_3$. The $CaCO_3$ content suggests that a substantial portion of the CaS reacted to form $CaCO_3$ and H_2S. However, no H_2S could be detected in the reactor off-gas by the analytical instrument although a strong odor of H_2S was noted in the sample gas stream.

In RED-REGEN-3, the calculated values for the bed composition were 62% $CaSO_4$, 26% CaS, and 12% $CaCO_3$. These data also suggest that H_2S should have been detected in the off-gas, although none was. In RED-REGEN-4, the final bed composition was 77% $CaSO_4$ and 23% $CaCO_3$.

After the completion of these two-step regeneration process studies, development studies in the 3-in.-dia unit were made on the one-step process ($CaSO_4 + CO \rightarrow CaO + SO_2 + CO_2$). This process required bed temperatures of ∿1950°F. A new method (combustion of kerosene plus CO, rather than pure CO) of reaching and maintaining the desired bed temperature was successfully demonstrated in two batch, reductive-decomposition experiments, REDUC-8 and -9. The operating procedure was as follows:

1. The fluidized bed was preheated to 900°F. Kerosene was then injected into the bed in a stream of carbon dioxide carrier gas and combusted with oxygen to increase the bed temperature.

2. When the bed was at temperature, the oxygen concentration in the off-gas was reduced to a value of 2%. Then carbon monoxide from a cylinder supply was introduced and was combusted along with kerosene to maintain the bed temperature and to provide the necessary reducing gas for the sulfate decomposition. Maximum allowable concentration of oxygen in the exit gas was 2%.

In REDUC-8, the bed temperature was maintained between 1500 and 1650°F to test the equipment, and in REDUC-9, the bed temperature was increased until a maximum of 1950°F was reached. In each experiment, the starting bed material was $CaSO_4$, the reactor pressure was ∿2 atm, and the superficial gas velocity through the bed was ∿3 ft/sec.

In both experiments, relatively large quantities of sulfur were removed from the $CaSO_4$ bed. In REDUC-8, 77% of the sulfur was removed in ∿3-1/2 hours, which is somewhat higher than expected. During the main part of the experiment, the CO and O_2 concentrations in the off-gas were ∿12 and ∿0.5%, respectively. The SO_2 concentration in the off-gas varied considerably, the maximum being 0.2%.

In REDUC-9, in which the bed temperature was gradually increased from 800 to 1950°F in a 3-1/2 hour period, about 97% of the sulfur was removed from the $CaSO_4$. The CO and O_2 concentrations in the exit gas were ∿3 and ∿1%, respectively. The maximum SO_2 concentration in the exit gas during the experiment was 1.1%.

The experiments have demonstrated a satisfactory procedure for increasing the bed temperature to the operating temperature and for maintaining this temperature. They also demonstrated that some release of sulfur from pure $CaSO_4$ particles can be achieved by the one-step regeneration technique.

An experiment (REDUC-12) was then made to regenerate, by the one-step technique, sulfated dolomite (Tymochtee) produced in a combustion experiment. The dolomite (6.1 wt % S) was regenerated at 1.7-atm pressure and an average bed temperature of 1950°F. The sulfated dolomite was fed to the fluidized bed throughout the experiment at a rate of 11.6 lbs/hr. Reductants for the reaction, mainly CO, CH_4, and H_2, were produced by the incomplete combustion of kerosene.(Pure CO was not added with the kerosene in this experiment.)

The sulfur dioxide concentration in the process off-gas averaged 1.1%, with a maximum peak of 2.1%. The H_2S content was ∿1% of the SO_2 content in the process off-gas. The calculated sulfur balance was 96%.

The particle-size distribution data for the feed material, the primary cyclone product, and the combined final bed and overflow products indicate that particle breakup occurred during the regeneration step.

Partial combustion of kerosene has been the method for obtaining the reducing gases required for most of the experiments made in the 3-in.-dia unit. In order to characterize the nature of the reducing gases formed, the concentration of reducing gases in the off-gas was measured during kerosene combustion in an inert fluidized bed at bed temperatures ranging from 1600-1900°F. The data showed that the CO and also the CH_4 concentrations in the off-gas varied directly with the kerosene/oxygen feed ratio.

Laboratory-Scale Regeneration Studies

Development studies on regeneration processes have continued using the 2-in.-dia, batch, fluidized-bed reactor employed in previous studies.[1] Aspects of the two-step and one-step regeneration processes have been investigated and a third scheme, a low-temperature (<1400°F) reaction of $CaSO_4$ with H_2 and CO_2 ($CaSO_4 + 4H_2 + CO_2 \rightarrow CaCO_3 + 3H_2O + H_2S$), has been studied. Data have also been obtained on the removal of H_2S from process off-gas using a permanganate solution.

Two-Step Process. Development studies of the two-step process have included a) cyclic experiments in which dolomite was sulfided with H_2S and the CaS reconverted to $CaCO_3$ using CO_2 and steam to determine if the absence of $CaSO_4$ (which had been present in previous cyclic experiments) affected the release of sulfur in the second step, b) scouting experiments of the effect of higher regeneration temperature on sulfur release, c) experiments using limestone (instead of dolomite as in previous experiments), d) effect of presence of hydrogen during second step on sulfur release, e) use of iron as a catalyst for reduction of $CaSO_4$ to CaS, f) a scouting experiment on a concept in which the two steps of the regeneration process are carried out at the same time in a single, staged reactor, and g) examination of particles from some of the experiments.

Cyclic Sulfiding-Regeneration Experiments. In previous attempts to convert sulfated additive ($CaSO_4$) to "pure" additive ($CaCO_3$) by the two-step process, the product has had a sulfur content that was too high for its reuse as an additive.[1] To determine whether undesirable side reactions occur between $CaSO_4$, CaS, and $CaCO_3$ that inhibit the removal of sulfur, experiments were made in which CaS was converted to $CaCO_3$ with the sulfate phase absent.

The experimental procedure consisted of partially calcining dolomite No. 1337 (to form $CaCO_3$ and MgO), reacting the $CaCO_3$ fraction with H_2S to form CaS, and converting the CaS to $CaCO_3$ by reaction with CO_2/H_2O. In previous experiments, $CaCO_3$ in dolomite had been reacted with SO_2 and the resulting $CaSO_4$ reduced partially to CaS before the CO_2/H_2O reaction.

In experiment CATS-22, a bed of dolomite No. 1337 was half-calcined at 1500°F with 40% CO_2-60% N_2 for 18 hours. The bed of $CaCO_3 \cdot MgO$ was then reacted at 1500°F and 2-3 atm with CO_2-N_2-H_2S for 30-60 minutes. The bed was reacted at 1100°F and 10 atm with an equimolar CO_2/H_2O mixture. This cycle was repeated three times. Sulfide concentrations in the bed after the CO_2/H_2O regeneration step of cycles 1, 2, and 3 were 6.5, 13.7, and 13.2 wt %, respectively. Before regeneration, the sulfide concentration was unknown for cycle 1 and was 21.1 and 16.7 wt % for cycles 2 and 3, respectively. Both the peak concentration of H_2S in the effluent gas stream during CO_2/H_2O regeneration and the regeneration time decreased in subsequent cycles. Apparently, the absence of sulfate does not improve the removal of sulfur because the same lower release of sulfur on cycling was noted as when sulfate was present. A sieve analysis of initial and final bed material and of fines collected in the filter chamber during the three cycles indicated that substantial attrition of bed particles occurred.

In experiment CATS-23, in which two cycles were completed, the reaction conditions were the same as in CATS-22 except that less sulfur was added to the bed in the H_2S addition steps, and H_2 was added to the CO_2/H_2O mixture during regeneration to prevent the possible formation of calcium polysulfides, which could interfere with sulfur release. The sulfur concentration in the bed material decreased from 5.8 wt % after H_2S addition to 2.9 wt % after regeneration for cycle 1 and from 6.5 wt % to 5.1 wt % in cycle 2. Approximately half of the sulfur present at the start was released in cycle 1 and only a fourth in cycle 2. Peak concentrations of H_2S were 16.1 and 13.9 vol % in cycles 1 and 2, respectively. Apparently, neither decreasing the quantity of sulfur in the bed nor adding H_2 to the regenerating gas mixture helped the sulfur removal in the second cycle.

Effect of Higher Regeneration Temperature on Sulfur Release. To determine if a higher temperature during the second or regeneration step would increase the removal of sulfur, experiment CATS-24 was performed at a regeneration temperature of 1250°F. The experimental procedure consisted of half calcining dolomite No. 1337 (calcination step) at 1500°F, reacting the $CaCO_3$ with H_2S in a mixture to form CaS (sulfiding step), and converting the CaS to $CaCO_3$ by reaction with CO_2/H_2O (regeneration step).

In experiment CATS-24, 1 kg of dolomite No. 1337 was calcined at 1500°F with 40% CO_2-60% N_2, forming a bed of $CaCO_3 \cdot MgO$. This material was reacted at 1500°F with CO_2-N_2-H_2S-H_2 until 25% of the $CaCO_3$ was converted to CaS. The bed of CaS, $CaCO_3$, MgO was reacted at 1250°F and 10 atm with 45% CO_2-45% H_2O-10% H_2 at a fluidizing-gas velocity of 1.4 ft/sec. The sulfur contents of the bed before and after the second or regeneration step were 6.2 and 2.5 wt %, respectively. These results represent a moderate increase over the highest sulfur removal achieved in the first cycle of the comparable CATS-23 experiment, in which the regeneration temperature was 1100°F.

The peak concentration of H_2S in the effluent gas stream during regeneration was 5.9 vol % (dry basis), which may be compared with an equilibrium H_2S concentration of $\sim$8 vol % (dry basis) at 1250°F.

Regeneration of Limestone. To determine if the composition of the additive has an effect on removal of sulfur, experiment CATS-26 was performed with limestone additive instead of dolomite additive (previously used). This experiment consisted of two cycles.

In the sulfiding step of each cycle of the experiment, limestone No. 1359 was reacted at 1500°F with CO_2-N_2-H_2S-H_2 until breakthrough of H_2S (H_2S addition step). In the regeneration step, the bed (now consisting of CaS and $CaCO_3$) was reacted at 1250°F and 10 atm with 45% CO_2-45% H_2O-10% H_2 (cycle 1) and with 50% CO_2-50% H_2O (cycle 2). The sulfur contents of the bed before and after regeneration in cycle 1 were 6.7 wt % and 5.2 wt %. During the regeneration step of cycle 2, the sulfur content of the bed stayed constant within analytical error at 10.8 wt %.

The peak concentrations of H_2S in the effluent gas stream during regeneration were 5.3 vol % (dry basis) in cycle 1 and 5.8 vol % (dry basis) in cycle 2. Sulfur removal was less in the cycles than that achieved with dolomite at identical experimental conditions.

Effect of Presence of Hydrogen During Second Step on Sulfur Release. The existence of possible intermediates such as polysulfides may interfere with the regeneration of partially sulfated additives. The presence of hydrogen during both stages of the regeneration process might prevent polysulfide formation. A bed of partially sulfated dolomite (15.4 wt % S) was reduced at 1600°F with H_2 as reductant for 5.5 hours. Conversion of $CaSO_4$ to CaS was essentially complete. The bed now containing ∿19% sulfide was reacted with 41.5% CO_2-41.5% H_2O-17% H_2 at 1200-1400°F for 52 minutes. The peak concentration of H_2S in the effluent gas stream at 1200°F was much less than the equilibrium concentration expected at that temperature. At 1400°F the equilibrium concentration (1.5%, dry basis) of H_2S was reached. The sulfide concentration was 16.8%, indicating that the presence of hydrogen does not markedly increase the conversion of CaS to $CaCO_3$.

Reduction of $CaSO_4$ Using CO and a Catalyst. The reduction of calcium sulfate to calcium sulfide with CO as reductant is catalyzed by the addition of Fe_2O_3 to the bed; a conversion of 97% at 1250°F after 45 minutes has been reported.[2] In an attempt to duplicate these results, a bed of partially sulfated dolomite was mixed by tumbling with 10% by weight of Fe_2O_3 powder and reacted with an equimolar mixture of CO-CO_2-N_2 at 1250°F for 4.5 hours. The conversion of $CaSO_4$ to CaS was 16.3% which is similar to results obtained with 100% H_2 at 1350°F.[1] The Fe_2O_3 did not effectively catalyze the conversion of $CaSO_4$ to CaS in dolomite at these conditions.

Two-Stage Reactor Concept. A modified regeneration process concept is discussed that utilizes a single-vessel, two-stage fluidized-bed reactor utilizing the two-step process to produce an off-gas containing H_2S and SO_2 at a mole ratio of two; this mixture would be suitable as feed to a Claus plant. The flow of solids and gas would be cocurrent in the reactor. The lower or reduction stage would be operated at 1800°F with a CO/CO_2 gas mixture. In this stage, SO_2 would be produced. Steam would be injected into the upper stage, and H_2S would be produced by reaction of CaS with H_2O/CO_2.

Examination of Bed Particles from Sulfation-Regeneration Experiments in Fluidized-Bed Reactors. Samples taken from several experiments performed in fluidized beds have been examined by optical microscopy, infrared spectroscopy, X-ray diffraction, and electron microprobe techniques as part of an effort to clarify the mechanisms associated with sulfation, reduction or sulfiding, and regeneration. The results were obtained on samples taken from the combustion, reduction, and regeneration steps of cycle two in a six-cycle, sulfation-regeneration experiment[1] and from CATS-22, a cyclic calcination-sulfiding-regeneration experiment. The six-cycle tests and CATS-22 were laboratory-scale experiments using dolomite 1337.

Material obtained from the second sulfation step in the six-cycle sulfation-reduction-regeneration experiment contained considerable sulfate, as indicated by X-ray and infrared spectrum analyses. The infrared spectrum also indicated the presence of some residual carbonate ($CO_3^=$) in this material and the X-ray data indicated the presence of some CaS. Careful examination of the electron microprobe scan made on a similar material (taken from the first sulfation step) showed that, in general, calcium and sulfur occurred together throughout a cross section of the particle at fairly uniform levels, whereas magnesium apparently was segregated from the calcium and sulfur. This observation was confirmed by X-ray data and indicated that sulfation took place throughout the particle and was not limited to a surface reaction.

The presence of iron on the particle surface, inferred from microscopic examination of the particles reported earlier,[1] was confirmed by the electron probe, which also showed some silicon and calcium on the surface of particles from the six-cycle test. The mineral form of this surface layer has not been identified. Microscopic examination of this surface layer on a hot stage indicated that its melting point was slightly less than 1100°C (2000°F).

In the infrared spectrum of material taken from the second reduction step of the sulfation-reduction-regeneration experiment, the intensity of the sulfate bands was much lower than after the sulfation step, as would be expected if calcium sulfate was indeed reduced to calcium sulfide, but the reaction was clearly not complete. The X-ray data indicated the same result. From the electron microprobe scan, it was not clear whether or not the conversion from sulfate to sulfide had been limited to a surface layer.

The most striking feature of the infrared spectrum and the X-ray data for material taken from the second regeneration step in the six-cycle sulfation-reduction experiment was the complete absence of sulfate. The carbonate feature in the infrared spectrum of this material was more prominent than in the previously discussed samples, and calcium carbonate could be detected in the X-ray pattern. The electron microprobe scan for material from the second regeneration step showed that calcium and sulfur appeared together uniformly across the particle, and that the iron-rich layer was still evident. Because all sulfate had disappeared at this stage of the process, the iron-rich layer apparently was not a barrier to reaction within the bulk of the particle.

Examination of the samples taken from CATS-22 showed that conversion of calcium carbonate to calcium sulfide by reaction with hydrogen sulfide did occur (although not all carbonate was converted in the sample examined); however, the regeneration reaction caused only partial conversion of sulfide to carbonate. Optical microscopy did not reveal a surface layer on any sample particles; electron microprobe scans were not made on the particles.

The results summarized above do not appear to explain directly the difficulties encountered in the regeneration process. It seems likely that an iron-containing layer forms on the particles during the sulfation process (in a bed where combustion is occurring and with sulfate or SO_2 involved in the layer-forming reaction), but that the layer is not directly responsible for the problems encountered in subsequent steps. The presence of sulfate after the reduction step and inability to effectively regenerate calcium sulfide in the CATS experiments suggest that the thermodynamics of the desired reactions may not be as favorable as previously believed, and that existing thermodynamic data should be re-examined to determine whether the present regeneration scheme is optimum.

One-Step Reductive Decomposition Process at Reduced Temperature. Data obtained using the 3-in.-dia regenerator had shown that high sulfur removals could be obtained even at temperatures as low as 1600°F. Previous work on the one-step process has been based on the understanding that temperatures above 1900°F were required. A program was initiated using the smaller 2-in.-dia unit to determine the conditions that have an effect on the removal of sulfur in a reduced-temperature, one-step process and to identify the vaporous sulfur species in the off-gas. A bed consisting of $CaSO_4$ (Drierite) was reacted at a bed temperature of 1200-1650°F with a gas composed of mixtures of CO and one or more of the following gases: CO_2, H_2O, O_2, and N_2. The data show that:

1. Regeneration appeared to be most effective when the bed temperature and CO_2 concentration were such that the calcium product was $CaCO_3$ rather than CaO.

2. Generally, high SO_2 concentrations were observed when the O_2 concentration was high.

3. The maximum concentrations of SO_2 and maximum sulfur removals were obtained with an inlet gas mixture consisting of 27% CO, 19% CO_2, 6% O_2, and the remainder nitrogen. The maximum SO_2 concentration was approximately equal to the equilibrium concentration expected for the reaction:

$$CaSO_4 + CO \rightarrow CaCO_3 + SO_2$$

4. Elemental sulfur was present in the off-gas, but the quantities detected were small.

5. Carbonyl sulfide was present in the off-gas. The concentration was small, except when high concentrations of CO (>30%) were used. The presence of carbonyl sulfide appeared to be dependent on the presence of sulfur dioxide.

Reaction of $CaSO_4$ and CO_2/H_2 at Temperatures of 1400°F and Less.

If the following reaction

$$CaSO_4 + 4H_2 + CO_2 \rightarrow CaCO_3 + 3H_2O + H_2S$$

proceeds at low temperatures, <1400°F, the concentration of H_2S in the off-gas is reasonably high. Equilibrium constants at 1000, 1200, and 1400°F are 4.37×10^8, 3.15×10^7, and 1.51×10^7, respectively. However, conversion of $CaSO_4$ to CaS ($CaSO_4 + 4H_2 \rightarrow 4H_2O$) must be avoided because the equilibrium concentration of H_2S for the reaction of CaS with CO_2/H_2O is low, less than 1500 ppm at 1400°F. A bed of $CaSO_4$ (Drierite) was reacted with 85% H_2-15% CO_2 at 10 atm and 1000, 1200, and 1400°F for 75, 135, and 120 minutes, respectively. The results indicate that:

1. The peak concentration of H_2S in the off-gas increases with temperature.

2. The sulfide content of the bed increases with temperature indicating that reduction of $CaSO_4$ to CaS is taking place, rather than conversion to $CaCO_3$.

3. At 1400°F, the peak concentration of H_2S (1160 ppm, dry basis) was nearly equal to the equilibrium concentration of H_2S (1460 ppm, dry basis) expected for the reaction between CaS and CO_2/H_2O, again indicating that the competing reaction in which CaS is formed is dominating.

Removal of H_2S from Off-Gas by Reaction with Potassium Permanganate. When CaS is converted to $CaCO_3$ by the reaction of CaS with CO_2/H_2O, H_2S will be formed. To avoid releasing H_2S into the laboratory exhaust system, a proposed scheme to remove the H_2S from the effluent gas stream is to pass the off-gas from the regenerator through a scrubber system containing potassium permanganate solution. The reaction expected to take place is

$$8KMnO_4 + 3H_2S \rightarrow 8MnO_2 + 3K_2SO_4 + 2KOH + 2H_2O$$

To determine if the above reaction occurs, as well as the contact time necessary for reaction, a laboratory-scale experiment was performed by passing a CO_2/H_2S gas mixture through a bubbler containing potassium permanganate solution and monitoring the effluent gas stream for H_2S with a quadrupole mass spectrometer.

The H_2S was readily reacted. As a result of these tests, $KMnO_4$ was used as the scrubber solution through which the regenerator off-gas was passed during an experiment.

Trace-Element Emission Studies

Studies have been initiated on the quantity and type of trace-element emissions from fluidized-bed combustors. Emissions from fluidized-bed combustors may be different than those from conventional combustors, owing to differences in operating variables such as combustion temperature and coal particle size. Comparisons with available data from conventional plants will be made.

In the bench-scale combustion equipment, a sampling system has been installed for collecting particulate and gaseous trace elements in the flue gas. Methods of analysis for the primary elements of interest (mercury, beryllium, lead, and fluorine) have been selected and analysis of test specimens has begun. A Brink impactor has been incorporated into the equipment so that the quantity and distribution of trace metals in particulate solids smaller than three microns can be determined.

II. INTRODUCTION

An experimental program is being carried out at Argonne National Laboratory (ANL) to develop advanced technology in pressurized, fluidized-bed combustion of coal and to investigate the effects of operating variables on combustion efficiency, sulfur retention efficiency, and NO_x and trace-element levels in the flue gas. Methods for the regeneration of the sulfated additive are being studied so that the additive can be reused in the combustor and the sulfur values recovered.

The concept of pressurized, fluidized-bed coal combustion entails the burning of coal at elevated pressure in a bed of additive (commonly, limestone or dolomite) that sorbs the sulfur released in the combustion. The capacity of the additive for sulfur retention is reduced by sulfation and it must be removed and replaced with fresh additive. However, it might be economically feasible to regenerate the additive for reuse in the combustor. The low temperature of combustion, as compared with higher temperatures in pulverized-coal boilers, may cause differences in the quantity and type of NO_x and trace-element pollutants leaving via the flue gas; hence, studies of both NO_x and trace-element emissions are also being made.

III. BENCH-SCALE, FLUIDIZED-BED, COMBUSTION-REGENERATION STUDIES

A. Materials

1. Coal

Two coals have been combusted in the 6-in.-dia fluidized-bed combustor: (1) an Illinois coal, obtained from the Peabody Coal Co., Christian County, Illinois, which has been designated Shipment No. 4; and (2) a bituminous coal obtained from Consolidation Coal Co., Arkwright Mine. The chemical characteristics and the particle-size distribution of these coals are listed in Tables 1 and 2, respectively.

Table 1. Chemical Characteristics of Coals

Illinois Coal, Seam 6, Mine 10, Peabody Coal Co.,
Christian County, Ill., Shipment No. 4

Arkwright Coal, Consolidation Coal Co., Arkwright Mine

	Proximate Analysis (wt %)			
	As Received		Dry Basis	
	Illinois	Arkwright	Illinois	Arkwright
Moisture	10.12	2.89		
Volatile Matter	37.90	38.51	42.17	39.66
Fixed Carbon	41.12	50.92	45.75	52.43
Ash	10.85	7.68	12.08	7.91
Sulfur	3.70	2.82	4.14	2.90
Heating Value, Btu/lb	10,956	13,706	12,163	14,114

	Ultimate Analysis (wt %)	
	Illinois	Arkwright
Carbon	66.96	77.14
Hydrogen	4.84	5.23
Sulfur	4.35	2.90
Nitrogen	1.33	1.66
Chlorine		0.19
Ash	13.50	7.91
Oxygen (no difference)	9.02	4.97

Table 2. Size Distribution of Coals

Illinois Coal, Seam 6, Mine 10, Peabody Coal Co.,
Christian County, Ill., Shipment No. 4

Arkwright Coal, Consolidation Coal Co., Arkwright Mine

U.S. Sieve No.	Sieve Analysis (wt %)	
	Arkwright Coal	Illinois Coal
+ 14		0.1
-14 + 25	8.0	14.5
-25 + 35	14.2	17.4
-35 + 45	12.3	12.0
-45 + 80	24.7	20.2
-80 + 170	17.9	13.6
- 170	23.0	22.2

2. Additive

A limestone (identified as No. 1359), obtained from the M.J. Grove Lime Co., Stephen City, Va., and a dolomite (Tymochtee), obtained from C. E. Duff and Sons, Huntsville, Ohio, are characterized in Tables 3 and 4. In operational testing of the regenerator, commercial $CaSO_4$ (Drierite) was used as a substitute for sulfated additive. Particle-size distribution for this latter material is presented in Table 4.

Table 3. Chemical Composition of Additives

Limestone No. 1359, M. J. Grove Lime Co., Stephen City, Va.

Tymochtee Dolomite, C. E. Duff and Sons, Huntsville, Ohio

Component	Chemical Analysis (wt %)	
	Limestone No. 1359	Tymochtee Dolomite
Ca	37.90	20.0
Mg	0.27	11.3
CO_2	NA[a]	38.5
H_2O	1.56	0.2
Derived		
$CaCO_3$	94.80	50.0
$MgCO_3$	0.95	39.1

[a] Not Available.

Table 4. Size Distribution of As-Used Additives

Limestone No. 1359, M. J. Grove Co., Stephen City, Va.

Tymochtee Dolomite, C. E. Duff and Sons, Huntsville, Ohio

Commercial $CaSO_4$ (Drierite)

	Sieve Analysis (wt %)		
U.S. Sieve No.	No. 1359 Limestone	Tymochtee Dolomite	$CaSO_4$
-7 + 14		0.1	70.5
-14 + 25	12.0	26.5	26.4
-25 + 35	23.2	21.4	1.1
-35 + 45	13.7	12.2	2.2
-45 + 80	26.8	18.3	
-80 + 170	8.1	9.8	
- 170	16.3	11.8	

3. Kerosene

Kerosene obtained from ANL stock was used in regeneration experiments as an energy source and, by its incomplete combustion, as a source of reductant gases (CO, H_2, and CH_4). The physical and chemical characteristics of ANL kerosene are given in Table 5.

Table 5. Chemical and Physical Characteristics of ANL Kerosene

Flash Point, Pensky-Martens, °F	119
Specific Gravity at 60/60°F	0.8086
Pounds per gal at 60°F	6.732
Specific Gravity, °API	43.5
Heating Value, Btu/lb	19,649
Btu per gal at 60°F	132,280
Sulfur, wt %	0.09

B. Equipment

Equipment has been installed for combusting coal at pressures up to 10 atm absolute and for regenerating sulfated lime for reuse. A simplified equipment schematic is shown in Fig. 1.

1. Pressurized, Fluidized-Bed Combustor

The pressurized, fluidized-bed combustor, shown schematically

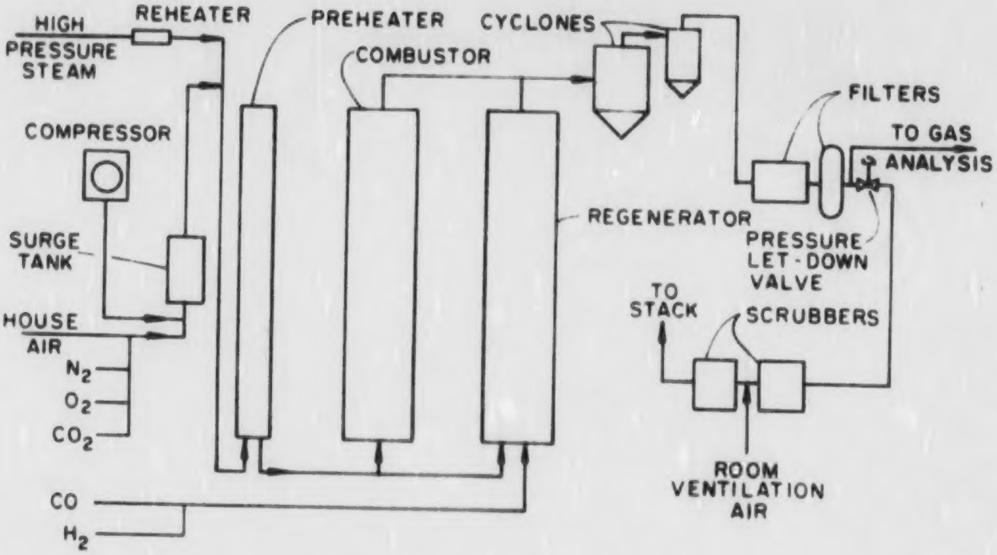

HIGH PRESSURE STEAM
REHEATER
PREHEATER
COMBUSTOR
CYCLONES
FILTERS
TO GAS ANALYSIS
COMPRESSOR
REGENERATOR
SURGE TANK
PRESSURE LET-DOWN VALVE
TO STACK
SCRUBBERS
HOUSE AIR
N_2
O_2
CO_2
CO
H_2
ROOM VENTILATION AIR

Fig. 1. Pressurized Combustion-Regeneration Equipment Schematic

in Fig. 2, consists of a 6-in.-dia schedule 40 pipe (Type 316 SS), approximately 11 ft long, contained within a 12-in.-dia schedule 10 pipe (Type 304 SS) over nearly the entire length. A bellows expansion joint is incorporated into the outer shell to accommodate differential thermal expansion between the pipes. The 6-in. pipe is alternately wrapped with 3/8-in.-dia, 3000-watt, resistance-type tubular heating elements and air-water cooling coils onto which has been applied a layer of heat-conducting copper and stainless steel spray. Sixteen heaters are attached to the unit, eight of which are connected to Variacs and temperature indicator-controllers. The controllers are activated by spring-loaded, coiled thermocouple assemblies which pass through the outer jacket and contact the heated pipe. Internal hairpin-shaped cooling coils of 3/8-in., schedule 40 pipe (Type 310 SS) extend down into the interior of the six-inch vessel from the flanged top to provide additional heat-transfer area. A water-air mixture is supplied to the internal and external cooling coils. Coolant flow is adjusted on the basis of the temperatures of the fluidized bed and the reactor wall.

A bubble-type gas distributor is flanged to the bottom of the inner vessel. Fluidizing air, thermocouples, solids feed lines, and solids take-off lines extend through the gas distributor (Fig. 3).

Coal and additive are pneumatically fed to the combustor by two 10-in.-dia, periphery seal, rotary valve feeders (Fig. 4), both of which are mounted on platform-type scales to indicate weight changes.

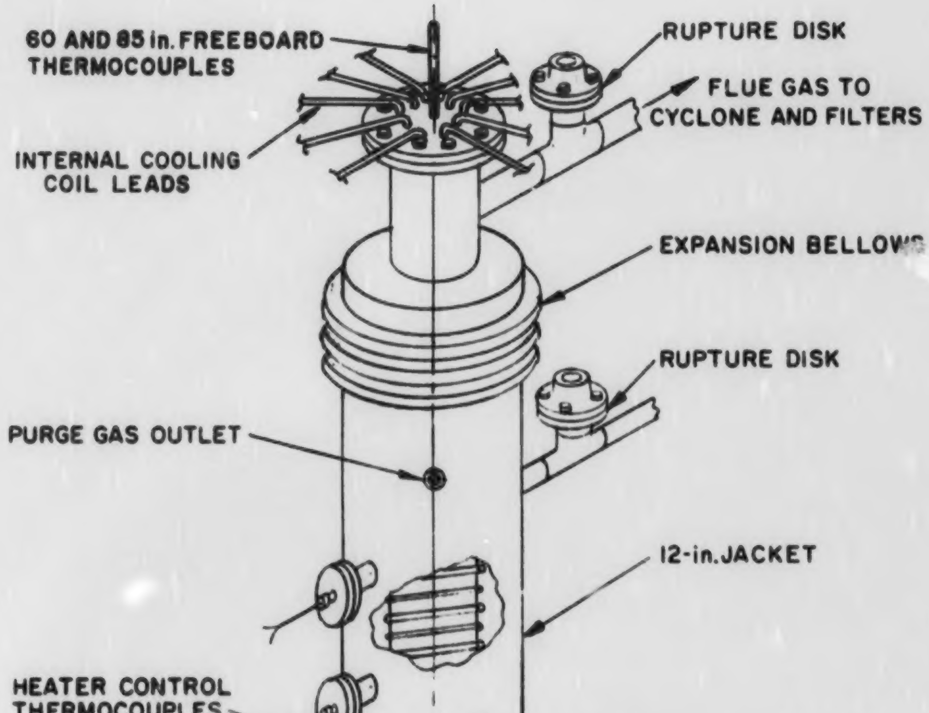

60 AND 85 in. FREEBOARD THERMOCOUPLES
RUPTURE DISK
FLUE GAS TO CYCLONE AND FILTERS
INTERNAL COOLING COIL LEADS
EXPANSION BELLOWS
RUPTURE DISK
PURGE GAS OUTLET
12-in. JACKET
HEATER CONTROL THERMOCOUPLES
EXTERNAL COOLING COIL (WRAPPED ON 6-in. DIA WALL)
CALROD TYPE HEATER
INTERNAL COOLING COILS
SHELL PURGE GAS INLET
BUBBLE CAP DISTRIBUTOR
EXTERNAL COOLING COIL LEADS
ELECTRICAL HEATER LEADS
PLIBRICO FILLED VOLUME
36 OR 48 in. SOLIDS OVERFLOW
SOLIDS FEED LINES
6, 12, AND 44 in. BED THERMOCOUPLE WELL
FLUIDIZING AIR

Fig. 2. Six-in.-Dia, Pressurized, Fluidized-Bed Combustor

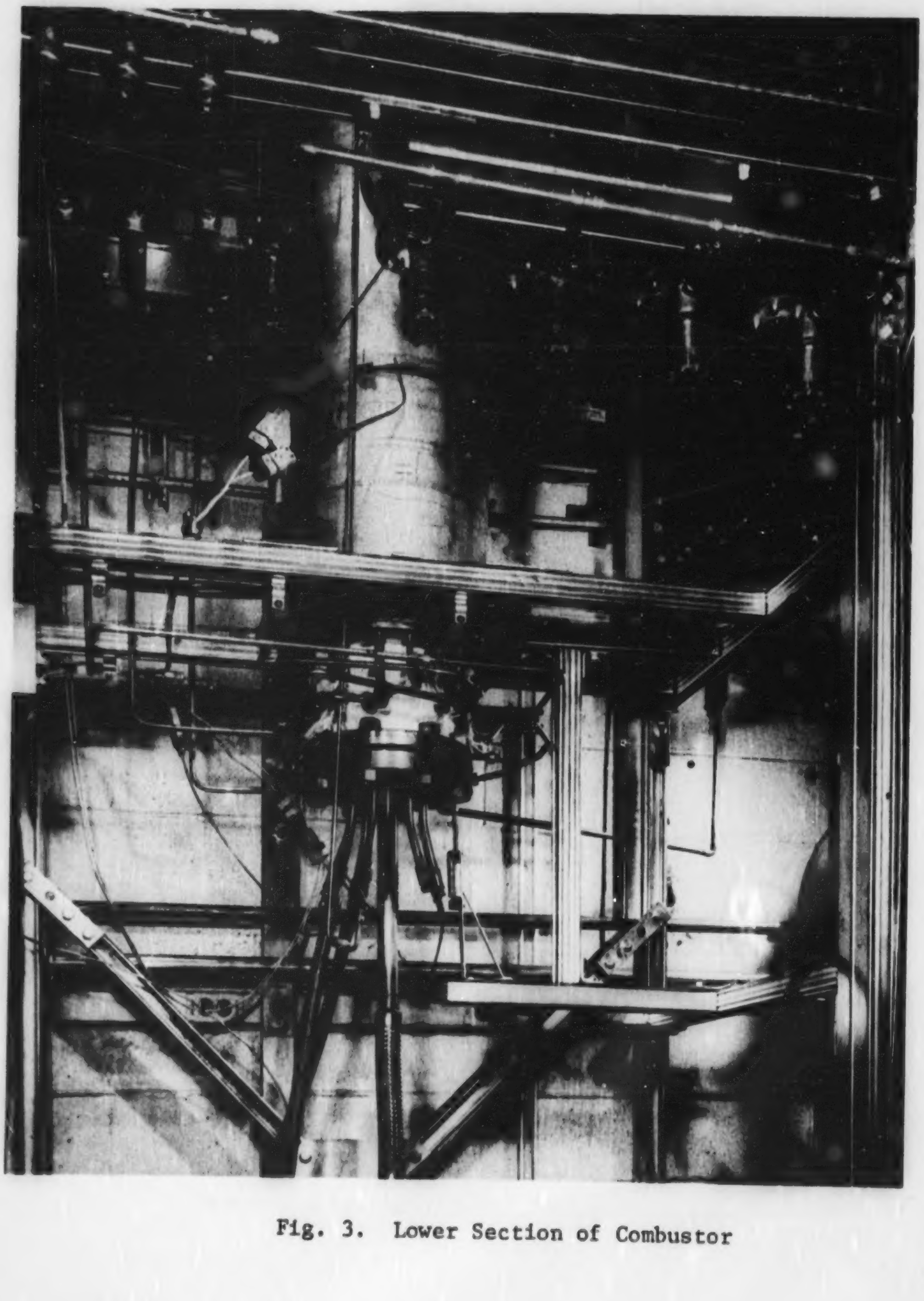


Fig. 3. Lower Section of Combustor

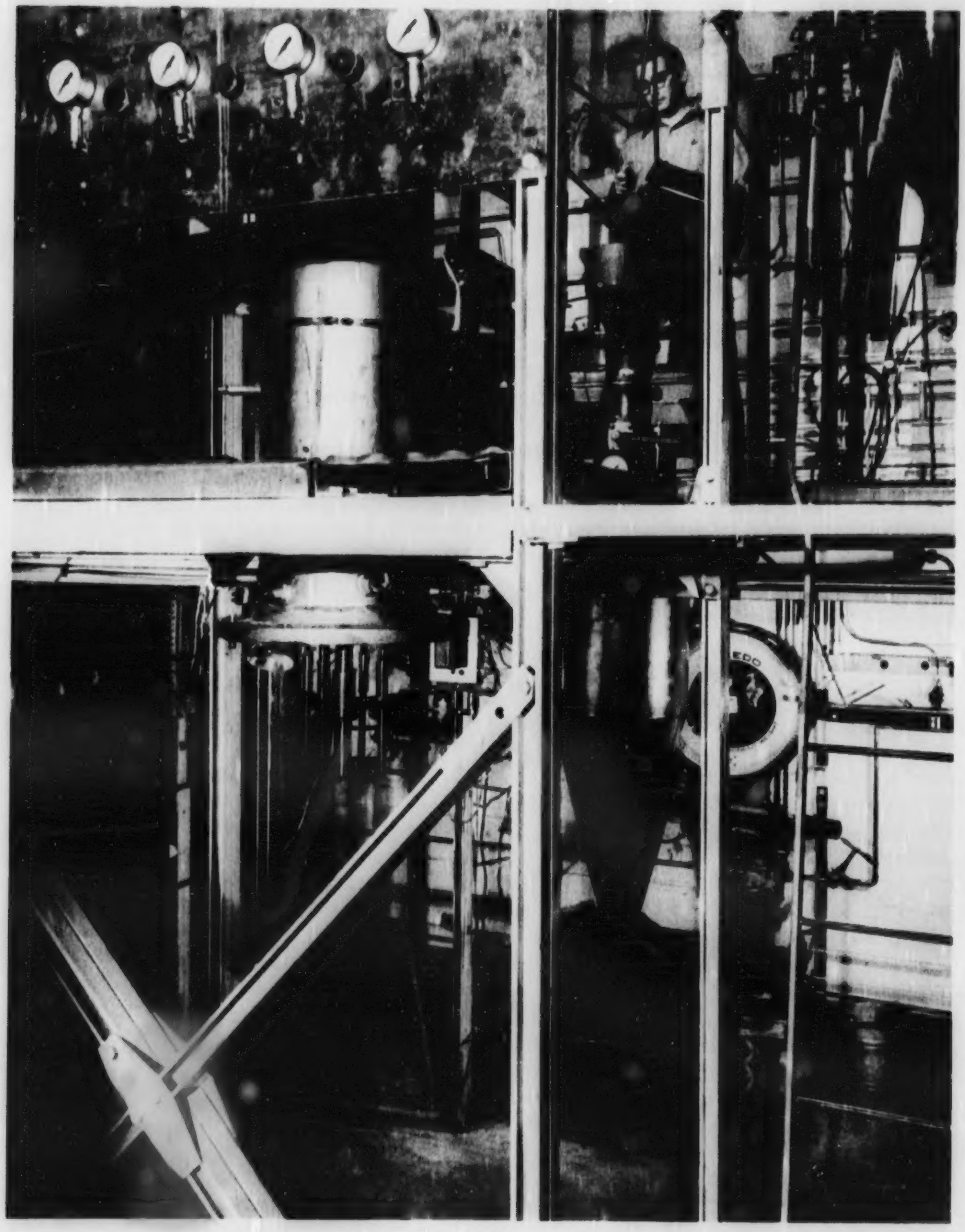


Fig. 4. Additive Hopper, Feeder, and Weigh Scale

A constant bed height is maintained in the combustor by use of either a 36-in. or 48-in. high overflow standpipe. Most of the fly ash and additive that is elutriated from the bed is removed from the flue gas by two cyclone separators in series. Essentially all of the remaining fines are removed by two Pall Trinity filters (in series), the first containing high temperature, epoxy-impregnated fiberglass elements, the second containing sintered metal elements. Both filters remove ∿95 wt % of +5 μm particle-size material. The flue gas is sampled downstream of the filters. An aliquot of the total flow is partially dried by passage through a water condensor and refrigerator and distributed to the gas analytical system where it is analyzed for SO_2, NO, CO_2, CO, CH_4, and O_2.

2. Fluidizing-Gas Supply System and 6-in.-dia Preheater

Fluidizing air for the combustor is supplied by a 75-hp, Gardner Denver, Electra-Screw compressor capable of delivering 100 cfm at 150 psig. The flow is metered by an orifice plate and flow recorder-controller assembly. The fluidizing air can be heated to approximately 1000°F by a 6-in.-dia preheater, shown schematically in Fig. 5. The gas preheater was designed in accordance with ASME code requirements and its design rating is 150 psig at 1500°F. Heat is supplied by eight 2700-watt, clam-shell-type heaters contained within a 4-1/2-in.-dia center pipe.

3. Fluidized-Bed Regenerator System

A 3-in.-dia fluidized-bed regenerator (shown schematically in Fig. 6), capable of operation at 150 psig and 2000°F, was constructed by casting a 2-1/2-in.-thick lining of Plibrico castable refractory in an 8-in.-dia, schedule 40, Type 316 stainless steel pipe. This entire assembly was enclosed by a pressure shell made of 12-in.-dia, schedule 20 carbon steel pipe. A bubble-cap-type gas distributor is connected to the bottom of the inner vessel via a slip fit, and held in place by retaining screws. Thermocouples, solids overflow lines, kerosene feed line, and bed drain line pass through the gas distributor and then through packing glands on the bottom flange of the outer vessel. The solids inlet line passes through the top flange of the unit and terminates above the bed. A nitrogen purge is supplied to the annular space between the inner and outer pipes and is maintained at a slightly higher pressure than the reaction zone to keep reactant gases from leaving the reaction zone.

The external wall of the inner vessel is wrapped alternately with eight 3000-watt, 0.315-in.-dia tubular resistance heaters and 3/8-in. OD by 1/16-in.-wall stainless steel tubing cooling coils over its entire length. High-temperature (∿550°C) heat-conducting putty was applied to the heaters and cooling coils and this layer was covered by an ∿1/2-in. layer of Fiberfrax rope. The heaters are controlled by temperature indicator-controllers and Variacs

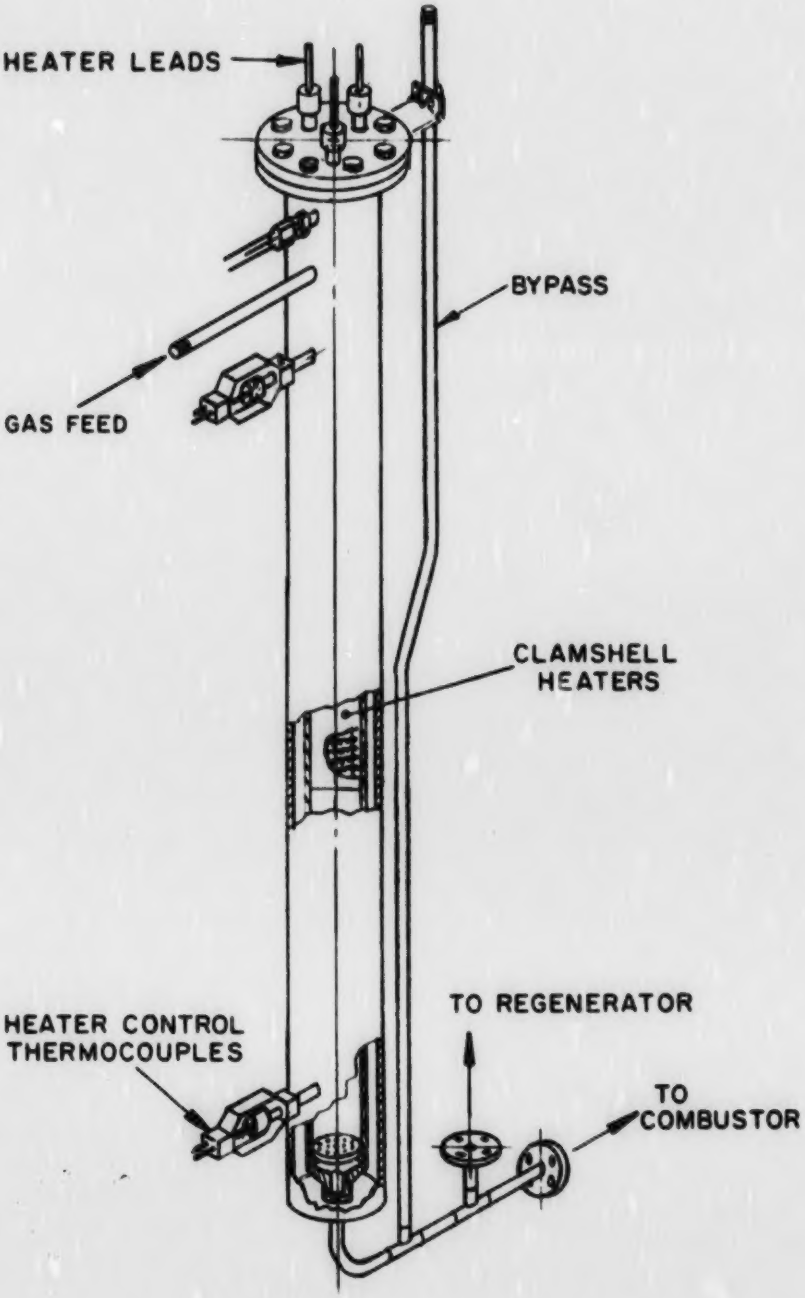

HEATER LEADS
BYPASS
GAS FEED
CLAMSHELL HEATERS
TO REGENERATOR
HEATER CONTROL THERMOCOUPLES
TO COMBUSTOR

Fig. 5. Six-in.-Dia, Fluidizing-Gas Preheater

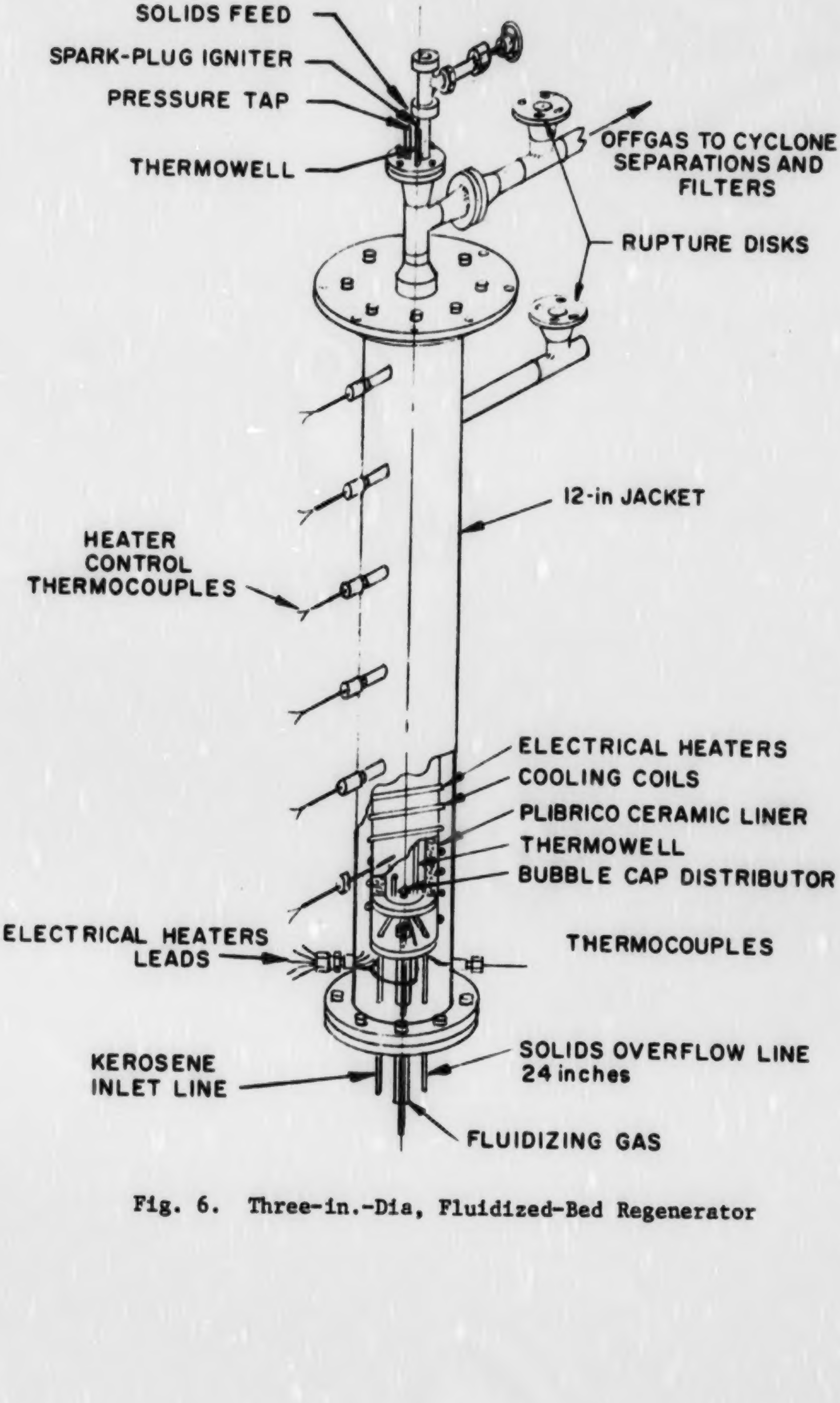

SOLIDS FEED
SPARK-PLUG IGNITER
PRESSURE TAP
THERMOWELL
OFFGAS TO CYCLONE SEPARATIONS AND FILTERS
RUPTURE DISKS
12-in JACKET
HEATER CONTROL THERMOCOUPLES
ELECTRICAL HEATERS
COOLING COILS
PLIBRICO CERAMIC LINER
THERMOWELL
BUBBLE CAP DISTRIBUTOR
ELECTRICAL HEATERS LEADS
THERMOCOUPLES
KEROSENE INLET LINE
SOLIDS OVERFLOW LINE 24 inches
FLUIDIZING GAS

Fig. 6. Three-in.-Dia, Fluidized-Bed Regenerator

actuated by thermocouples that are in spring-loaded contact with the inner vessel wall of the regenerator. Cooling-water flow is manually controlled.

Reactant gases are delivered from high-pressure gas cylinders and metered by use of orifice-plate flow recorder-controller assemblies. All gases, with the exception of oxygen and carbon monoxide, are preheated in the 6-in.-dia preheater prior to distribution through the bubble-cap distributor. Oxygen is introduced into this heated gas stream at a point just prior to its passage through the bottom flange of the regenerator. Carbon monoxide is introduced directly into the bed via a separate line. Both the inner vessel and annular space are protected by the use of rupture disks and pressure relief valves.

Sulfated additive is pneumatically fed to the regenerator via the solids inlet line by one of the two 10-in.-dia, periphery seal, rotary valve feeders (see Fig. 4).

Off-gas and entrained solids from the regenerator are processed by the cyclone-filter system common to the combustor, which has been described above.

Fig. 7 shows an overall view of the pressurized combustion-regeneration pilot plants.

4. Analytical Equipment

A schematic of the process-gas sampling and analysis system associated with the fluidized-bed combustor is shown in Fig. 8. Approximately 1% (1.0 scfm) of the total flue gas is withdrawn at a point immediately after the secondary filter. Using system pressure, this stream is passed through a water condenser, a sintered-metal bayonet filter (to remove solids), and then through a refrigerated condenser for additional water removal. Any residual water, which could interfere with the measurement of flue-gas constituents by an infrared technique, is removed by magnesium perchlorate. (Approximately 3000 ppm moisture would give an infrared analyzer reading corresponding to ∿20 ppm NO. Carbon monoxide and methane analyses would also be affected by moisture).

Continuous determinations of NO and SO_2 are carried out using Beckman Model 315A infrared analyzers, and continuous analysis of CH_4 and CO with Mine Safety Appliance (MSA) Model MRA infrared analyzers. A Hays paramagnetic oxygen analyzer (Model 632) provides continuous measurement of oxygen. Intermittent CO_2 analyses are performed using a Hewlett-Packard Model 700 gas chromatograph.

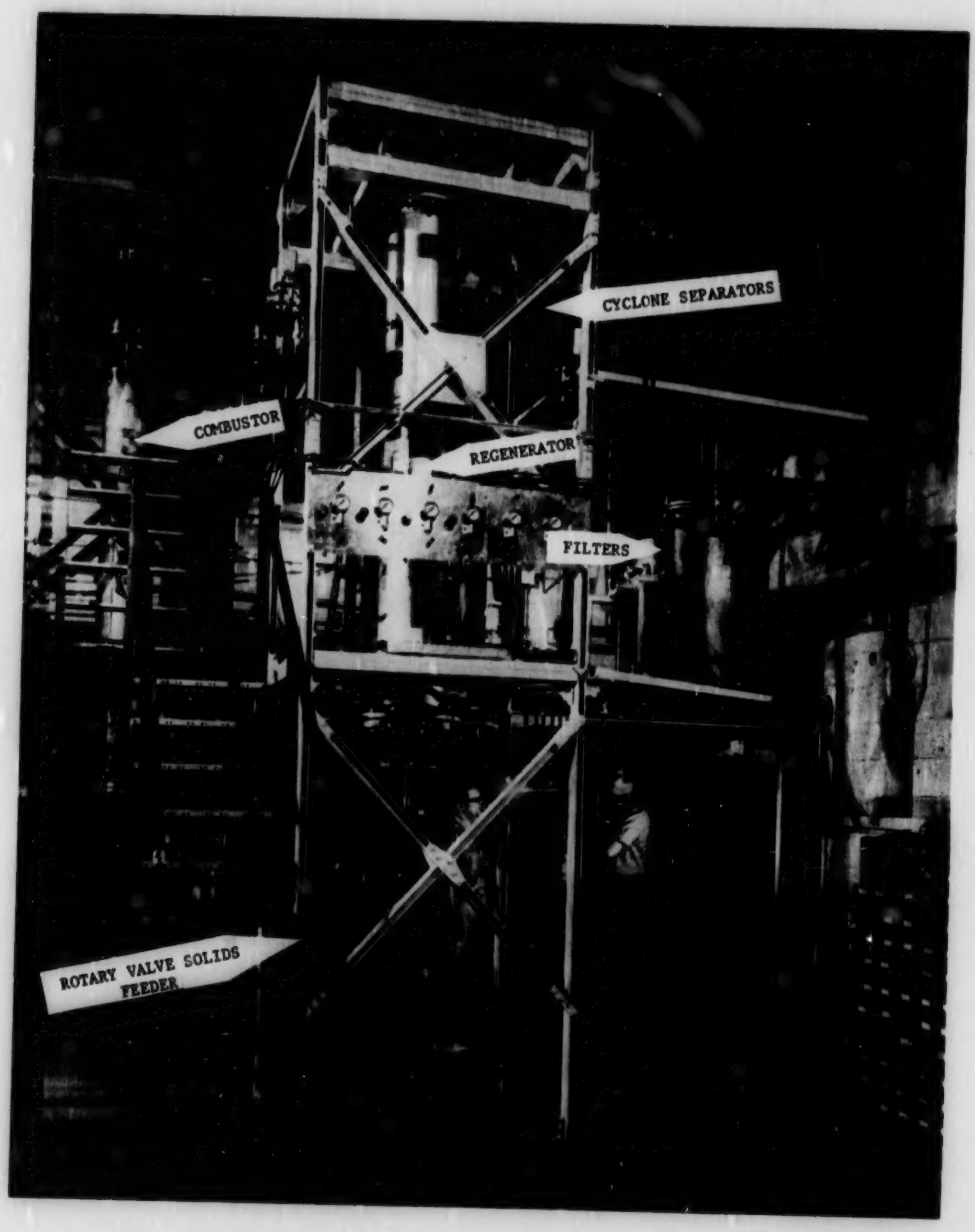

CYCLONE SEPARATORS
COMBUSTOR
REGENERATOR
FILTERS
ROTARY VALVE SOLIDS FEEDER

Fig. 7. Combustion and Regeneration Pilot Plants

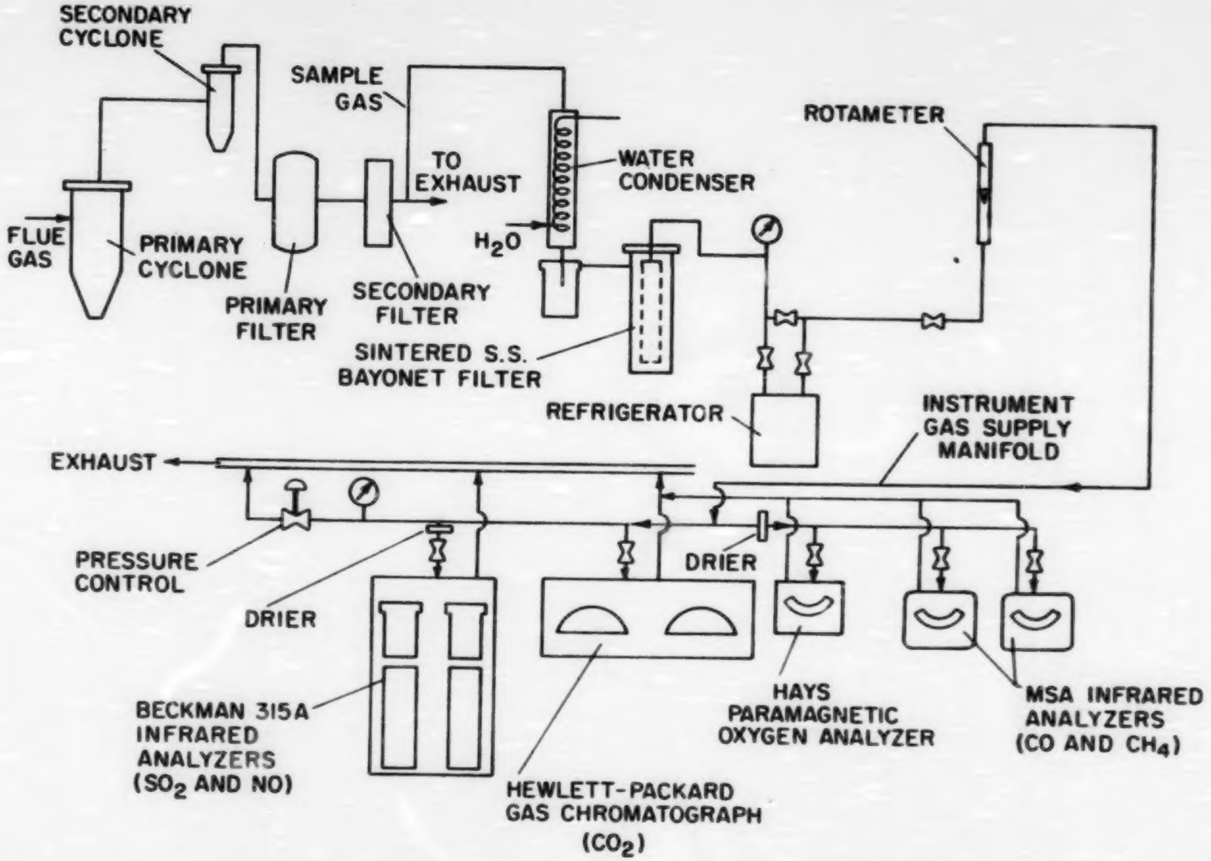

SECONDARY CYCLONE
SAMPLE GAS
ROTAMETER
TO EXHAUST
WATER CONDENSER
FLUE GAS
PRIMARY CYCLONE
H_2O
PRIMARY FILTER
SECONDARY FILTER
SINTERED S.S. BAYONET FILTER
REFRIGERATOR
INSTRUMENT GAS SUPPLY MANIFOLD
EXHAUST
PRESSURE CONTROL
DRIER
DRIER
BECKMAN 315A INFRARED ANALYZERS (SO_2 AND NO)
HEWLETT-PACKARD GAS CHROMATOGRAPH (CO_2)
HAYS PARAMAGNETIC OXYGEN ANALYZER
MSA INFRARED ANALYZERS (CO AND CH_4)

Fig. 8. Gas Sampling and Analysis System

Each of these instruments is supplied with sample gas through a pressurized manifold maintained at constant pressure. Individual gas streams supply each instrument and are controlled by flow valves in each line. Prior to and during each experiment, the response of each analytical instrument is determined using standard gas mixtures of flue-gas components in nitrogen. If required, instrument zero and span adjustments are made. The analytical equipment components are listed in Table 6.

Specific analytical procedures used on solid samples obtained after an experiment are listed in Appendix B.

C. Coal Combustion Experiments

In addition to a series of shakedown experiments, which were performed to gain familiarity with the newly installed pressurized combustor and which are not reported, a coal combustion experiment at atmospheric pressure was performed in the new unit using limestone additive to compare results with those previously obtained at ANL in the atmospheric-pressure equipment.[1] This was followed by a high-pressure combustion experiment using Tymochtee dolomite additive.

1. Comparison of SO_2 Retention in Old and New Combustion Units

The new combustor was operated at atmospheric pressure, and the data on SO_2 retention and NO level obtained were compared with data obtained in the previously installed atmospheric-pressure combustor. The intent was to determine whether differently designed combustion zones in the two combustors would contribute to marked differences in SO_2 and NO levels in the flue gas. Pertinent differences in design are the following:

	Previously Installed Combustor	Newly Installed Combustor
Coolant tubes in bed	None	Five hairpin tubes occupy a maximum of 10% of the cross-sectional area
Injection of coal and additive into the fluidized bed	Perpendicular to the fluidizing-gas flow	Parallel to the gas flow and up into the bed
Removal of sulfated solids from the bed	Intermittent, through a line at the bottom of the bed	Continuous, through a vertical standpipe whose top is 36 in. above the gas-distributor plate

Table 6. Flue-Gas Analytical Equipment

Flue-Gas Constituent	Method of Analysis	Instrument Model	Output Displayed On	Range	Accuracy (% of range)
Sulfur Dioxide	Infrared	Beckman 315A	Bristol, two-pen, variable-range recorder	0-5000 ppm 0-10,000 ppm	±1%
Nitric Oxide	Infrared	Beckman 315A	Bristol, two-pen, variable-range recorder	0-500 0-1000 ppm	±1%
Oxygen	Paramagnetism	Hays 632	Honeywell-Electronik 17, 2-pen, 0-10 mV range recorder	0-1 vol % 0-10 vol %	±2%
Methane	Infrared	MSA LIRA 200	Honeywell-Electronik 17, 2-pen, 0-10 mV range recorder	0-1000 ppm	±1%
Carbon Monoxide	Infrared	MSA LIRA 300	Honeywell-Brown Electronik, variable range	0-5000 ppm	±1%
Carbon Dioxide	Gas Chromatography	Hewlett-Packard 700	Honeywell-Electronik 16, variable chart speed, reversed-drive recorder	0-20 vol %	±5%

In this experiment (SD-11), the operating procedure used in the newly installed combustor was similar to that used in the previously installed combustor. The partially sulfated limestone and alumina bed was heated to a temperature at which coal would ignite. Following ignition, coolant was supplied to the coolant tubes as necessary to control the bed temperature. Illinois coal (see Table 1) and No. 1359 limestone were premixed, and the mixture was air-conveyed to the bed. Premixing was necessary because the rates that would be required for separate feeding were less than the minimum feed rates of the newly installed solids feeders.

Operating conditions and steady-state flue gas concentrations for Experiment SD-11 are presented in Table 7. The flue gas SO_2 level was 420 ppm, which corresponds to ∿89% retention of sulfur in the bed. This retention is similar to the sulfur retention expected if the previously installed atmospheric combustor had been operated at the same conditions (*i.e.*, at a Ca/S mole ratio of 3.5, see Fig 9). The flue gas NO level was within the range (300-600 ppm) expected for coal combustion experiments conducted under similar conditions. The conclusion is that the design differences in the combustors did not markedly affect the results.

2. High-Pressure Operation

An experiment (ARK-3) has been performed in which Arkwright coal was combusted in the 6-in.-dia pressurized combustor at 9.3 atm absolute. The fluidized-bed temperature was maintained at ∿1515°F, the superficial gas velocity was ∿2.5 ft/sec, and Tymochtee dolomite was fed at a Ca/S mole ratio of 3.

The as-received dolomite was double-screened prior to use as the starting bed and feed material. All of the +14 mesh fraction was removed to eliminate particles that might be difficult to air-transport to the combustor and some of the -100 mesh particles were removed because these would have elutriated rapidly from the bed. The particle size distribution of the feed and product materials are shown in Table 8.

In starting up the combustor, the bed in the combustor and the fluidizing gas were preheated to ∿850°F. Coal was then injected into the bed and burned to bring the bed temperature up to ∿1500°F. When this bed temperature had been established, the system pressure, which had been 6 atm absolute, was increased to 9.3 atm absolute.

Table 9 lists the operating conditions and the results of the experiment. The average SO_2 concentration in the flue gas was 100 ppm, indicating that over 95% of the sulfur in the coal was retained by the additive. For comparison, SO_2 removals of 78 and 87% were achieved in two atmospheric pressure experiments (BC-2 and -3) conducted in the previously installed combustor using Tymochtee dolomite additive and an alumina starting bed.[3]

Table 7. Operating Conditions and Results for Experiment SD-11

Equipment: ANL 6-in.-dia, fluidized-bed, pressurized combustor

Coal: Illinois Seam No. 6, Peabody Coal Co., 3.7 wt % S (-14 mesh)

Additive: Limestone No. 1359, as received (94.80 wt % $CaCO_3$, 0.95 wt % $MgCO_3$)

Starting Bed: Partially sulfated and calcined limestone No. 1359 (3.2 kg) plus
30-mesh Alundum (4.8 kg)
(~24-in. starting fluidized-bed depth)

Bed Temp (°F)	System Pressure (atm)	Coal Feed Rate (lb/hr)	Additive Feed Rate (lb/hr)	Feed Ca/S Mole Ratio	Superficial Fluidizing-Air Velocity (ft/sec)	Steady-State Flue-Gas Concentrations					SO_2 Retention (%)
						O_2 (vol %)	CO_2 (vol %)	CO (ppm)	NO (ppm)	SO_2 (ppm)	
1470	~1.1	5.0	2.0	3.5	2.8	2.7	16.8	250	375	420	89

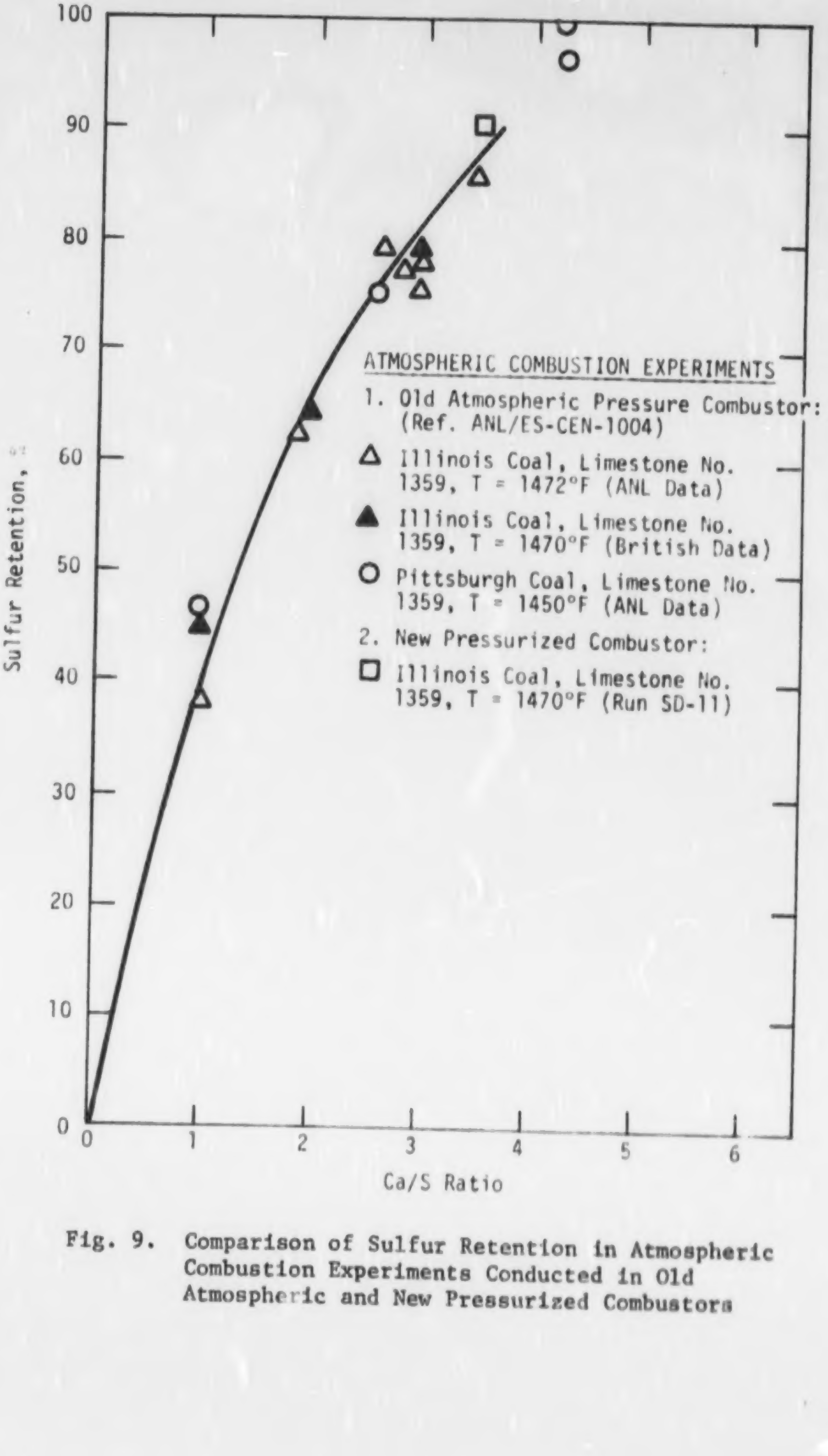


Fig. 9. Comparison of Sulfur Retention in Atmospheric Combustion Experiments Conducted in Old Atmospheric and New Pressurized Combustors

Table 8. Particle-Size Distribution of Feed and Product Materials for Experiment ARK-3

	Sieve Analysis (wt %)		
U.S. Sieve No.	Tymochtee Dolomite, As Fed	Arkwright Coal, As Fed	Sulfated Bed Overflow and Final Bed
+ 14	0.1		0.5
-14 + 25	26.5	8.0	46.0
-25 + 35	21.4	14.2	32.4
-35 + 45	12.2	12.3	15.3
-45 + 80	18.3	24.7	5.8
-80 + 170	9.8	17.9	
- 170	11.8	23.0	
Avg. Particle Size, μm	531	323	772

Operating conditions for these latter experiments consisted of a bed temperature of 1600°F, a gas velocity of 3 ft/sec, a bed depth of 2 ft, and a nominal Ca/S mole ratio of 1.5. The NO concentration in the flue gas during ARK-3 averaged 170 ppm, which is roughly half of that found in the atmospheric-pressure combustion experiments. Approximately 90 pounds of sulfated additive was obtained.

D. Regeneration of $CaSO_4$

When coal is burned in a fluidized bed containing limestone or dolomite additive, the product of the reaction between sulfur-containing gases and additive is calcium sulfate if combustion is carried out under oxidizing conditions or calcium sulfide if combustion is carried out with a deficiency of air. As the capacity of the bed material to retain sulfur is approached, bed material must be removed from the combustor and replaced with fresh material. Simply discarding the sulfur-bearing material would be unattractive because of (1) the cost of replacement material, (2) the cost of transporting fresh material to the furnace and used materials from the furnace, (3) disposal costs, and (4) pollution problems associated with the disposal of used material (especially if it contained calcium sulfide, which would slowly release hydrogen sulfide if exposed to air). A process for regenerating used bed material so that the lime may be recycled through the combustor is needed, both to circumvent these problems and to recover the sulfur value as sulfuric acid or elemental sulfur.

Several regeneration processes have been considered. If the product of the reaction between sulfur-containing gases and additive in the combustor is calcium sulfate, the processes are

Table 9. Operating Conditions and Results for Experiment ARK-3

Equipment:	ANL 6-in.-dia, fluidized-bed, pressurized combustor
Coal:	Arkwright, Consolidation Coal Co., 2.82 wt % S (-14 mesh)
Additive:	Tymochtee Dolomite, C. E. Duff and Sons, Huntsville, Ohio (50.0 wt % $CaCO_3$, 39.1 wt % $MgCO_3$)
Starting Bed:	6.5 kg Tymochtee dolomite (-14 mesh) (~15-in. starting, fluidized-bed height)
Fluidizing-Gas Velocity:	~2.5 ft/sec

Bed Temp (°F)	System Pressure (atm)	Coal Feed Rate (lb/hr)	Additive Feed Rate (lb/hr)	Feed Ca/S Mole Ratio	Average Flue-Gas Concentrations					
					O_2 (vol %)	CO_2 (vol %)	CO (ppm)	NO (ppm)	CH_4 (ppm)	SO_2 (ppm)
1515	9.3	22.4	14.0	3.4	3.7	18.0	249	108	103	100

1. Thermal decomposition of calcium sulfate to form CaO and SO_2.
2. Reductive decomposition of calcium sulfate to form CaO and SO_2.
3. Reductive decomposition of calcium sulfate to form CaS, followed by process 1 or 2 below.

If the product of the reaction is calcium sulfide, the processes are

1. Roasting of calcium sulfide in air or oxygen to form CaO and SO_2.
2. Reaction of calcium sulfide with steam and carbon dioxide to form $CaCO_3$ and H_2S.

The sulfur dioxide or hydrogen sulfide formed would then be converted to sulfur in a Claus plant or to sulfuric acid in a conventional acid plant to recover the sulfur value.

During the past year, the bench-scale reactor (3-in. dia) has been used to perform preliminary investigations of potential regeneration methods. It has also been used in the initial stages of cyclic combustion-regeneration experiments to determine the effects of recycle under different operating conditions on the performance of the additive.

1. Two-Step Regeneration Experiments

A two-step regeneration process was investigated which involved the reduction of calcium sulfate to calcium sulfide with carbon monoxide in the first step and subsequent reaction of the calcium sulfide with carbon dioxide and steam to form $CaCO_3$ in the second, or actual regeneration, step. The chemical equations for the two reactions are as follows:

$$1/4\ CaSO_4 + CO \rightarrow 1/4\ CaS + CO_2 \qquad (1)$$

$$CaS + CO_2 + H_2O \rightarrow CaCO_3 + H_2S \qquad (2)$$

Both steps were investigated in the 3-in.-dia, bench-scale regenerator. Four reduction experiments (RED-1, -2, -3, and -4) were performed, and with the exception of the first reduction experiment, each was followed by a CO_2/H_2O regeneration experiment (REGEN-2, -3, and -4) using the reduced material from the preceeding RED experiment. The experiments were carried out during the initial testing of the new equipment at which time the primary objective was to test the operation of the regenerator at pressures up to 10 atm absolute.

Drierite ($CaSO_4$) was the starting-bed material in these batch experiments. Gases for reduction and regeneration were taken from either high-pressure cylinders or building supply sources. Arkwright coal was burned in the bed during Experiment RED-4 to increase the bed temperature.

In the reduction run, 2.4 or 3.5 kg of calcium sulfate (Drierite) was charged to the regenerator, and the height of the settled bed was 2 or 3 ft, respectively. Heated fluidizing air or nitrogen was passed through the bed to increase the temperature to approximately 1000°F. In RED-1, -2, and -3, a mixture of 5% C_2H_2 - 2% O_2 in nitrogen was then fed to the reactor to increase the bed temperature from 1000 to 1700°F. In RED-4, Arkwright coal was injected and combusted in the bed in place of the acetylene. In all four experiments, carbon monoxide was then substituted for the hydrocarbon and the bed was maintained at ∿1700°F by burning the carbon monoxide with oxygen. Enough excess CO was fed to allow for the reduction of the calcium sulfate. The pressure in the regenerator, initially near atmospheric, was then increased to the operating pressure. Run time for the four RED experiments was 3 to 5 hours.

To start a REGEN run, the CO combustion was stopped by shutting off the CO and O_2 feeds and the temperature of the bed was allowed to drop to ∿1100°F from the reduction process temperature of 1700°F. Carbon dioxide, diluted with nitrogen, was passed through the bed, and then steam was added to this mixture. Bed temperature was maintained at ∿1000°F for 1 hr during the subsequent regeneration step.

Experiments were conducted at pressures of 8, 30, 75, and 135 psig in this equipment-testing phase of the investigation. The operating conditions and the outlet-gas concentrations for the experiments are presented in Tables 10a and 10b.

Samples were taken of the final bed after the two steps had been completed and were analyzed for sulfide and total sulfur content. No sulfide (<0.3%) was found in the sample from RED-1, which contained 18.0% total sulfur. This may have been caused by the relatively high oxygen concentration in the bed.

In RED-1, as well as the three succeeding RED experiments, some sulfur was released from $CaSO_4$ as SO_2 by the one-step reductive decomposition reaction:

$$CaSO_4 + CO \rightarrow CaO + SO_2 + CO_2 \qquad (3)$$

Bed temperatures were high enough at times for this to occur. In RED-2 and RED-3, oxygen concentration was carefully controlled (oxygen concentration in the exit gas was kept at a minimum), and sulfide was formed in the bed. After RED-REGEN-2, 37% of the sulfur was present as sulfide (S_{total} = 20.2% and $S^{=}$ = 7.5%) and in the third experiment, 44% of the sulfur was present as sulfide (S_{total} = 26.2%

Table 10a. Summary of Operating Conditions, Bench-Scale, Batch Regeneration Experiments, Two-Step Process

Experiment	Starting Bed Material	Feed Material	System		Gas Velocity (ft/sec)	Input Flow Rates				
			Temp (°F)	Pressure (psia)		O_2 (scfm)	CO (scfm)	H_2O (scfm)	CO_2 (scfm)	N_2 (scfm)
RED-1	2.4 kg $CaSO_4$ (-7+25 mesh)	None	1700	22.7	∿3.3	0.45-0.67	1.33			1.6
RED-2	2.4 kg $CaSO_4$ (-7+25 mesh)	None	1560-1800	28.7	∿3.5	0.28-0.48	0.56-1.8			2.4-2.8
REGEN-2	Final Bed from RED-2	None	1060-1140	36.7	∿1.3			0.7	2.2	
RED-3	3.5 kg $CaSO_4$ (-7+25 mesh)	None	1630-1890	75	∿3.0	0.45-1.1	2.8-3.3			5.9-8.2
REGEN-3	Final Bed from RED-3	None	1000-1090	75	∿2.3			0.52	5.5-6.4	5.0
RED-4	2.4 kg $CaSO_4$ (-7+25 mesh)	None	1310-1950	150	Varied	Varied	1.9-2.5			5.3
REGEN-4	Final Bed from RED-4	None	900-930	127	∿0.9			0.63	2.2	5.3

Table 10b. Summary of Operating Conditions and Results, Bench-Scale, Batch Regeneration Experiments, Two-Step Process

	Outlet-Gas Concentrations							Analysis of Final Bed or Overflow		
Experiment	O_2 (vol %)	CO_2 (vol %)	CO (vol %)	SO_2 (ppm)	NO (ppm)	CH_4 (ppm)	Solids Sulfur Removal (%)	$S^{=}$ (wt %)	Total Sulfur (wt %)	Purpose
RED-1	0.6-0.9	30	2-13	0-730	0-710	75	~29	<0.3	18	Two-Step Process Studies
RED-2	0.1-0.15	22.5[a]	16.3->26	375-2730	35-45	300-400	ND[b]	ND	ND	
REGEN-2	0.1-0.15	33[a]	1.8-2.6	325-430	0-5	250-300	~31	7.5	20.2	
RED-3	0.3-0.7	18-23	10-19.6	420-2250	20-33	150-200	ND	ND	ND	
REGEN-3	0-0.15	18.2-46.6	0.01-0.11	25-80	10-30	20-50	~13	11.6	26.2	
RED-4	0-0.05	<10	2.4-18	25-65	20	200-300	ND	ND	ND	
REGEN-4	0.05	ND	ND	80	ND	200	ND	ND	ND	

[a] One determination.

[b] Not determined.

and $S^{=}$ = 11.6%).

Analysis showed that the starting $CaSO_4$ bed material in these experiments was relatively pure. Based upon Ca and S analyses, the final bed from RED-REGEN-2 contained 54% $CaSO_4$, 17% CaS, and 29% $CaCO_3$, if it is assumed that the sample of bed contained only (1) unreacted $CaSO_4$, (2) CaS made in the reduction step, but not converted to $CaSO_4$ by steam/CO_2, and (3) $CaCO_3$ from the steam/CO_2 reaction with CaS. The $CaCO_3$ content suggests that a substantial portion of the CaS was reacted to form $CaCO_3$ and H_2S in the second step. However, no H_2S could be detected in the reactor off-gas using the quadrupole mass spectrometer analysis method, even though a strong odor of H_2S was noted in the sample gas stream. The instrument readings during this and the other experiments are therefore considered suspect.

In RED-REGEN-3, the calculated values for the bed composition were 62% $CaSO_4$, 26% CaS, and 12% $CaCO_3$. These data also suggest that H_2S should have been detected in the off-gas during REGEN-3, but none was detected.

In RED-REGEN-4, the final bed composition was calculated to be 77% $CaSO_4$ and 23% $CaCO_3$. As in previous experiments, H_2S should have been detected during REGEN-4, but again, none was detected.

From the data obtained in these experiments, it was concluded that the experimental system will be operable at design conditions. Certain modifications were made to the equipment, however, in an attempt to provide better temperature control and reduce the oxygen concentrations in the gas phase to very low levels. The modifications include (1) adding a spark ignition source inside the regenerator unit and substituting kerosene for acetylene and (2) relocating the oxygen inlet line so that, in the reduction step, the CO and O_2 mix before they enter the bed. In the above investigation, CO was added directly to the bed and the oxygen added to the gas stream upstream from the preheater.

2. One-Step Regeneration of $CaSO_4$, Batch Operation

After the completion of the two-step regeneration studies, the emphasis on regeneration methods shifted to the one-step process, which requires higher temperatures than the reduction step of the two-step process. The one-step process is based on the following chemical reaction:

$$CaSO_4 + CO \rightarrow CaO + SO_2 + CO_2$$

Two experiments involving the batch reduction of calcium sulfate (Drierite) were completed to test a procedure for bringing the fluidized bed to process temperature and maintaining that temperature by combusting kerosene and CO.

In the first experiment, REDUC-8, which was a test experiment, a 1650°F bed temperature was maintained rather than a higher temperature required for reductive decomposition. In the second experiment, REDUC-9, a temperature of 1950°F (required for the one-step process) was attained.

The operating procedure consisted of the following steps:

1. The fluidized bed was heated to 900°F. Kerosene was then injected into the bed in a stream of CO_2 carrier gas and combusted in the preheated, fluidizing-air stream to increase the bed temperature to 1600°F.

2. When the bed was at temperature, the oxygen flowrate was reduced until its concentration in the off-gas was less than 2%. CO from cylinder sources was then added. Bed temperature was then adjusted to the temperature required in the experiment.

The starting-bed material was $CaSO_4$ (Drierite) in each of the two batch experiments conducted at 2 atm absolute pressure. No $CaSO_4$ was added to the bed during the experiments and kerosene combustion was continued throughout the experiments.

In REDUC-9 the CO concentration was purposely kept low (as was the CO/CO_2 ratio) to maximize the SO_2 concentration in the off-gas. Operating data for these experiments are shown in Tables 11a and 11b.

The bed temperature, the inlet gas and kerosene flowrates, and the measured outlet-gas concentrations in REDUC-8 and REDUC-9 are plotted in Figs. 10 and 11, respectively. Superficial gas velocities in the regenerator averaged 2.5 and 3.3 ft/sec for REDUC-8 and -9, respectively.

Analyses of samples of material removed from the final bed of each experiment showed that sulfur removal was high. The weight of sulfur in the $CaSO_4$ starting bed for REDUC-8 was 535 g. Of this weight, 67 g (12.5%) of the sulfur remained in the final bed. Calculated composition of the final bed was 12.2% CaS, 5.2% $CaSO_4$, 82.6% $CaCO_3$ (S_{total} = 5.40%; $S^=$ = 4.19%). Thus, 87.5% of the initial sulfur in the $CaSO_4$ was removed in about 3-1/2 hr at a 1500-1600°F bed temperature. The average SO_2 concentration in the off-gas during this period was 0.1%. Only 42 g (7.8%) of the initial sulfur left the system as SO_2. The remaining 426 g (79.7%) of the initial sulfur was unaccounted for. This latter material might have left the system in the form of COS, H_2S, or elemental sulfur in the off-gas. The concentrations of these off-gas constituents were not determined. The high level of sulfur removal that resulted at the relatively low operating temperature was unexpected.

The weight of sulfur in the $CaSO_4$ starting bed for REDUC-9 was also 535 g. Of this weight, 5.7 g (1.1%) of the sulfur remained in the final bed. Calculated composition of the final bed was 0.3%

Table 11a. Summary of Operating Conditions, Bench-Scale Regeneration Experiments, One-Step Process

Experiment	Type	Starting Bed Material	Feed Material	Feed Rate (lb/hr)	System		Gas Velocity (ft/sec)	Input Flow Rates				
					Temp (°F)	Pressure (psia)		O_2 (scfm)	Kerosene (cc/min)	CO (scfm)	CO_2 (scfm)	N_2 (scfm)
REDUC-8	Batch	$CaSO_4$ 2.27 kg	None		1300-1650	29.4	~2.3	0.2-1.1	6.8-22.0	0-1.4	0.7-2.9	1.4-2.1
REDUC-9	Batch	$CaSO_4$ 2.27 kg	None		850-1950	24.7	~3.3	0.3-0.6	0-22.0	0-0.1	0.5-1.6	1.4-1.6
REDUC-10	Cont.	$CaSO_4$ 2.27 kg (-7+25 mesh)	Same	4.0	1720-1920	29.7	5-6	0.6	23	0-1.4	0.1-0.3	2.2-3.5
REDUC-12	Cont.	Sulfated Tymochtee Dolomite 2.72 kg (6.1% S)	Same	11.6	1950	25	3.0	1.7	31.6		0.1	2.1
REDUC-13	Cont.	$CaSO_4$ 2.40 kg (-7+25 mesh)	Same	6.0	1724 1500 1455	41	2.4 2.7 2.4	0.6 0.4 0.4	23.3 29.3 23.3		3.9 5.0 5.0	1.0 1.0 0.8

Table 11b. Summary of Operating Conditions and Results, Bench-Scale Regeneration Experiments, One-Step Process

Experiment	Type	Outlet-Gas Concentrations O_2 (vol %)	 CO_2 (vol %)	 CO (vol %)	 SO_2 (ppm)	 NO (ppm)	 CH_4 (ppm)	Approx. Solids Sulfur Removal (%)	Analysis of Final Bed or Overflow $S^=$ (wt %)	 Total Sulfur (wt %)	Purpose	Comments
REDUC-8	Batch	0- 11.5	41- 51	2.5- 15.0	100- 1900	30- 440	40- 9900	77	4.2	5.4	One-Step Process Studies	Test of 1-Step Process Conditions
REDUC-9	Batch	0- 3.2	47[a]	1.5- 6.0	0- 10000	50- 785	2000- 10000	97	0.1	0.6		
REDUC-10	Cont.	0.02- 4.5	7.2- 19.3	1.0- 6.8	0- 42400	25- 820	0- 6800	85	2.5	7.5		Continuous Feeding Test
REDUC-12	Cont.	1.3	28.4	4.1	11000	166	7900	59	0.06 (Overflow)	3.9		Regeneration Step, Cycle 1 of Cyclic Study
REDUC-13	Cont.	1.8 1.5 1.4	82 86 86	5.2 4.3 4.3	1400 1500 1100	274 610 620	14000 20000 20000	12	0.07 (Overflow)	21.5		Effect of High CO_2 Conc.

[a] One determination.

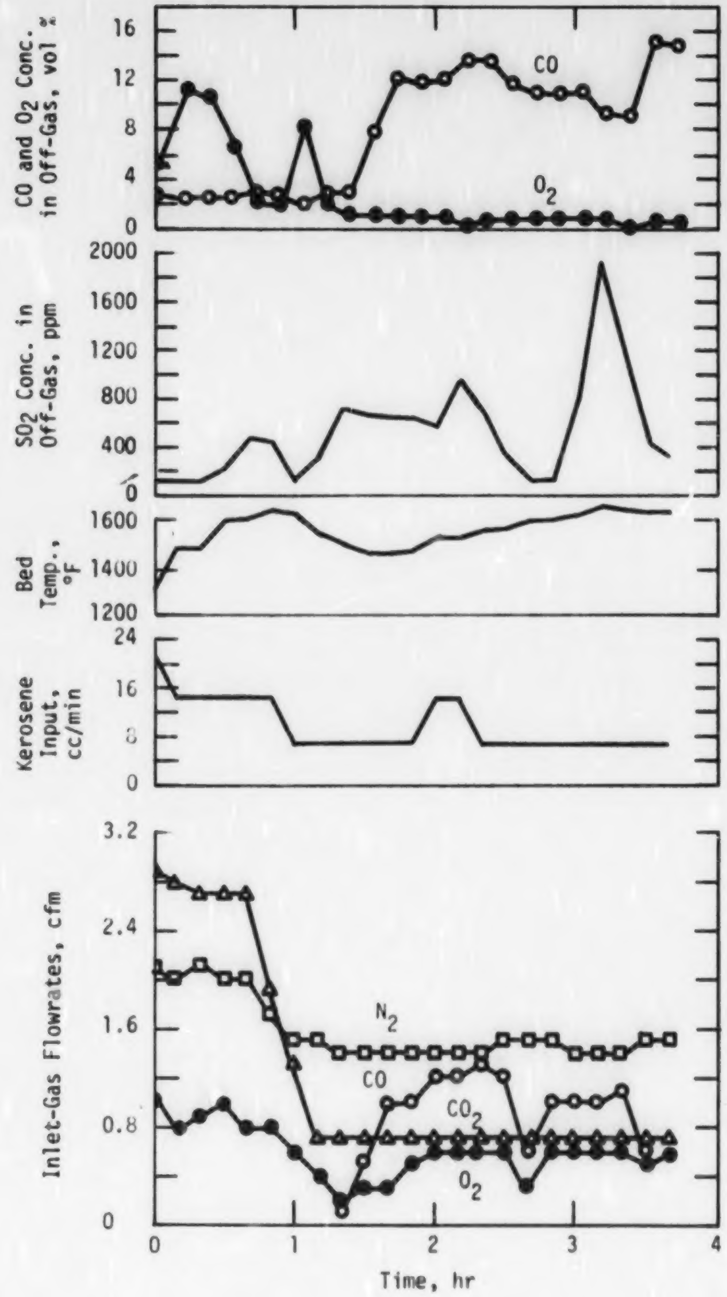


Fig. 10. Conditions and Results for Experiment REDUC-8 (Pressure: 2 atm absolute)

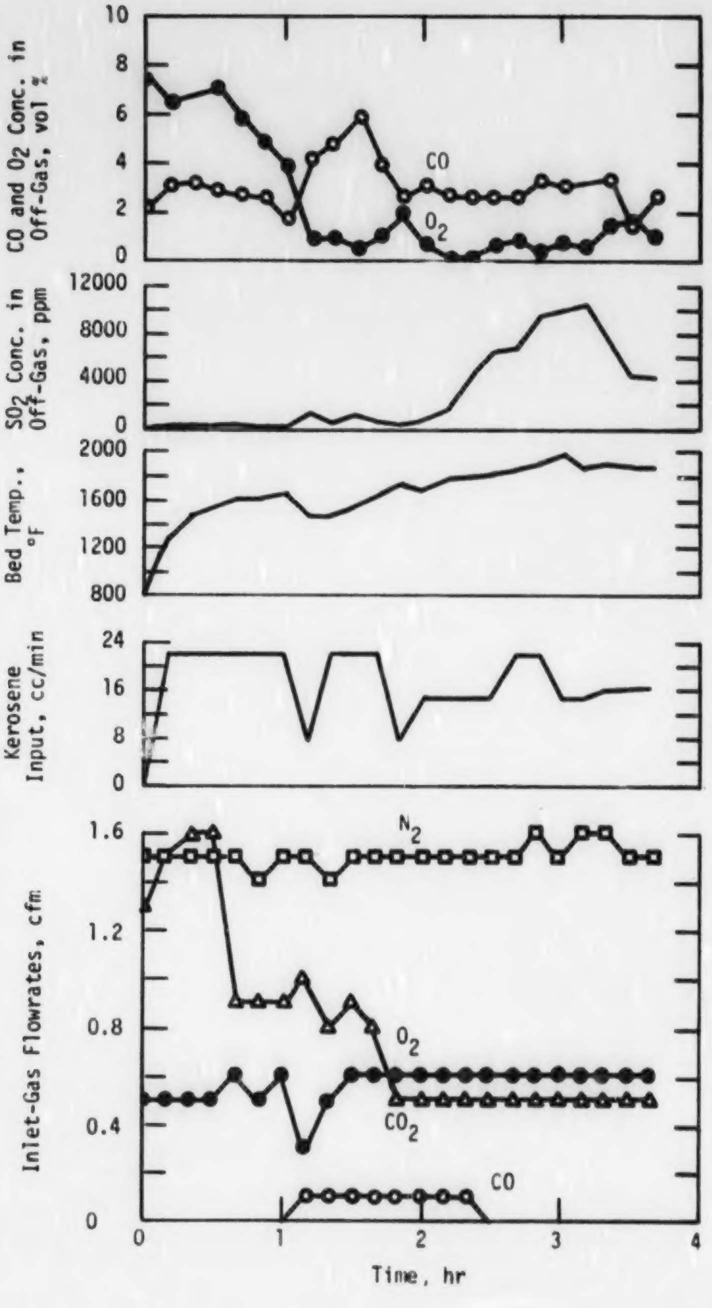


Fig. 11. Conditions and Results for Experiment REDUC-9 (Pressure: 2 atm absolute)

CaS, 2.0% $CaSO_4$, and 97.7% $CaCO_3$* (S_{total} = 0.62%; $S^=$ = 0.14%). Thus, 98.9% of the initial sulfur in the $CaSO_4$ was removed in about 3-1/2 hr at a 1600-1900°F bed temperature. In this experiment, the bed temperature was higher but the CO concentration was lower than in REDUC-8. The average SO_2 concentration in the off-gas was 0.24%. Only 75 g (14.0%) of the initial sulfur left the system as SO_2. The remaining 454 g (84.9%) of the initial sulfur was unaccounted for. The form of this latter material is unknown. Data from the quadrupole mass-analysis unit showed a slight blip where the H_2S peak would be expected, but the H_2S concentration could not be measured because the peak was too small. No COS peak was noted. It is possible that elemental sulfur vapor was produced and condensed in the off-gas stream.

3. One-Step Regeneration of $CaSO_4$, Continuous Operation

A single one-step regeneration experiment (REDUC-10) was made in which the $CaSO_4$ was fed continuously to the regenerator. In this experiment, the starting bed material and the solids fed to the regenerator bed during the experiment were $CaSO_4$ (Drierite).

In the startup procedure, the fluidizing gas was preheated and the solids in the fluidized bed were heated by electrical heaters until a bed temperature was reached sufficient to combust kerosene (~800°F). By burning kerosene, the bed temperature was then increased to the experimental operating temperature of ~1900°F. After about one hour (with the bed at 1900°F), $CaSO_4$ was fed into the bed at a rate of 4 lb/hr. Pressure in the system was 15 psig, and the fluidizing-gas velocity was 5-6 ft/sec. The bed temperature, the inlet gas and kerosene flow rates, and the concentrations of the gases exiting from the bed† are shown in Figs. 12 and 13 (see also Tables 11a and 11b).

Both SO_2 and H_2S were present in the process off-gas. The SO_2 concentration generally ranged between 1 and 4% while $CaSO_4$ was being fed. The maximum SO_2 concentration recorded was ~6%. The H_2S concentration was not measured continuously, as was the SO_2

---

* $CaCO_3$ assumed rather than CaO because the bed was cooled in a CO_2 gas stream after the experiment.

† The concentration of the off-gas constituents exiting the bed are calculated values. In regeneration experiments with continuous additive feed, gas leaving the fluidized bed is diluted with additive transport gas and the concentrations of the off-gas constituents are measured after the combined gases leave the regenerator. The concentration of a particular off-gas constituent above the bed is then calculated by multiplying its concentrations in the diluted stream by the ratio of the flow rates in the diluted and undiluted streams.

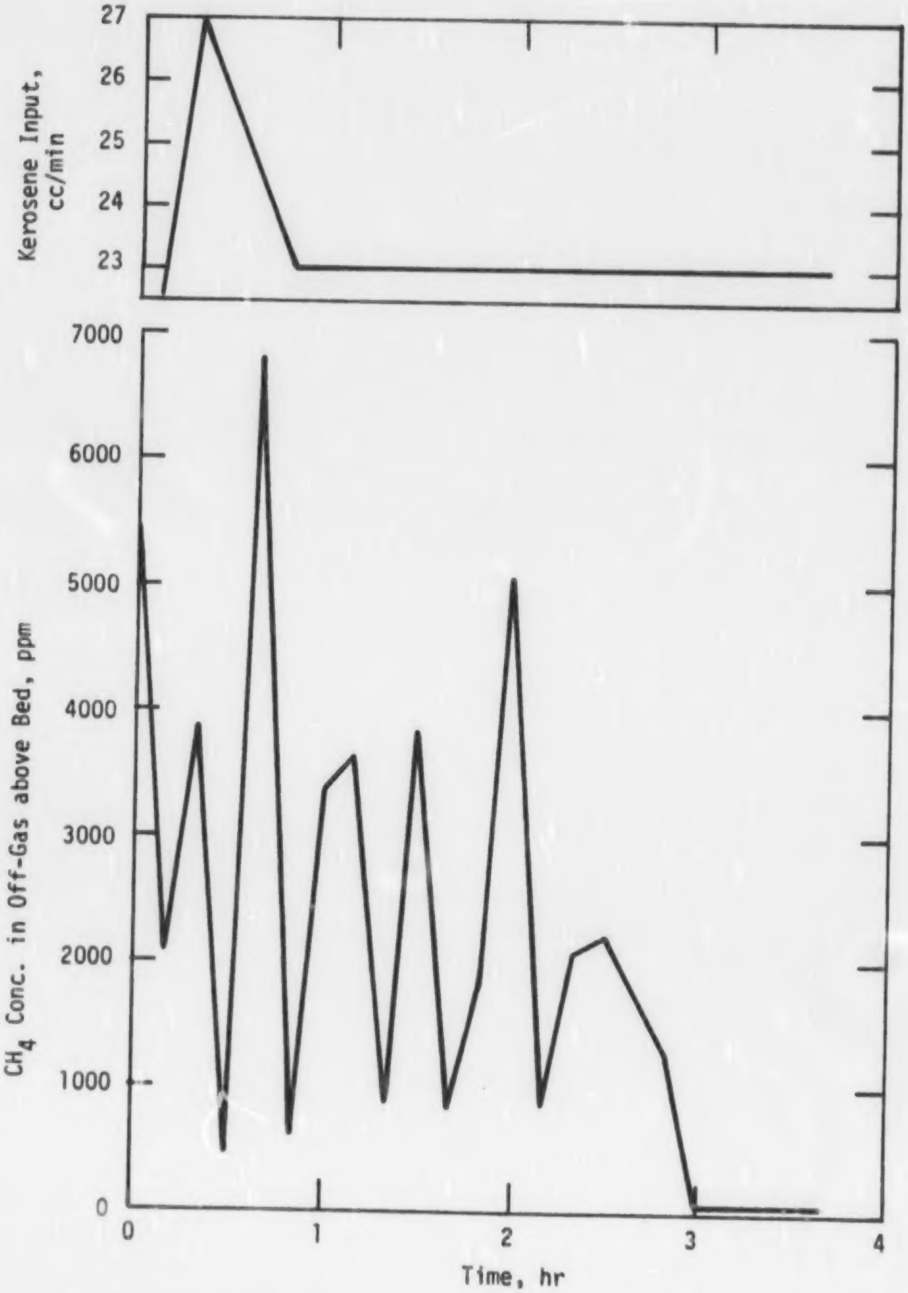


Fig. 12. Kerosene Input and CH$_4$ Concentration in Process Off-Gas for Experiment REDUC-10

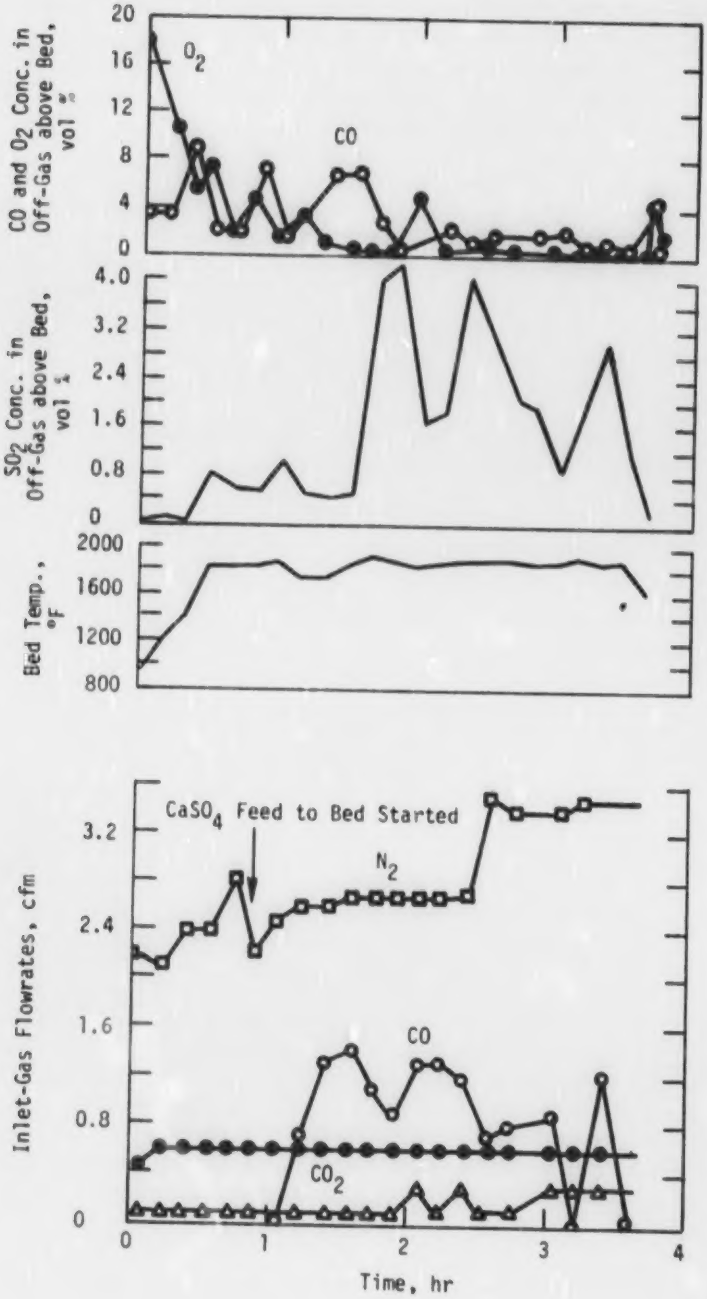


Fig. 13. Conditions and Results for Experiment REDUC-10 (Pressure: 2 atm absolute)

concentration. The total H_2S content of the process off-gas was obtained by analyzing the quantity of CuS residue in a copper sulfate solution through which a proportionate part of the process off-gas was passed. Based on this analysis, the sulfur, as H_2S, was approximately 20% of the sulfur found in the process off-gas.

The sulfur material balance, presented in Table 12, shows that a little over 60% of the sulfur was accounted for. One source of the unaccounted sulfur is the very fine particulate matter in the off-gas that was not collected in the cyclone separators. Other unrecovered sulfur might have been in the form of elemental sulfur that deposited in process lines by the H_2S-SO_2 reaction. Thorough cleanup of the off-gas piping system would recover this sulfur.

Table 12. Sulfur Balance for Experiment REDUC-10

IN:	Sulfur, kg
$CaSO_4$, Starting Bed	0.51
$CaSO_4$, Fed during Experiment	1.03
TOTAL IN:	1.54
OUT:	
Final Bed	0.08
Cyclone Solids	0.12
Off-Gas: As SO_2	0.59
As H_2S	0.16
TOTAL OUT:	0.95
DEFICIT:	0.59 or 38%

The solids removed from the regenerator after the experiment contained 73% CaO, 21% $CaSO_4$, and 6% CaS. No product (*i.e.*, no overflow from the bed) was collected in the product container during the experiment. A considerable quantity of solids (about 20 wt % of the starting bed plus fed solids) was collected in the cyclone receivers. These solids consisted of about 80 wt % $CaSO_4$ and 20 wt % CaO. Lower (less than 5-6 ft/sec) fluidizing-gas velocities would result in less of the solids being elutriated from the bed.

4. One-Step Regeneration of Sulfated Dolomite, Continuous Operation

An experiment (REDUC-12) was completed in which the sulfated Tymochtee dolomite (6.1 wt % S) produced in combustion experiment ARK-3 was used as the feed. The regeneration was carried out at 1.7 atm absolute pressure and an average bed temperature of 1950°F.

Sulfated dolomite was fed to the fluidized bed throughout the experiment at a rate of 11.6 lbs/hr, and the resultant solids overflow from the bed was collected by use of the internal 24-in.-high standpipe. Reductants for the reaction, mainly CO, CH_4, and H_2, were produced entirely by the incomplete combustion of kerosene within the bed. No separate addition of CO was made as had been done in past experiments. Kerosene also was the energy source for elevating the bed temperature from the 700°F preheat temperature to the operating temperature of 1950°F.

Operating conditions and results for this experiment are shown in Tables 11a and 11b. The oxygen flow to the bed was controlled so that the oxygen concentration in the off-gas was maintained at less than 1.5%, which resulted in the presence of reducing gases in the off-gas. The CO and CH_4 concentrations in the off-gas above the bed[*] averaged 4.1 and 0.8%, respectively. Hydrogen concentration was not measured. The SO_2 concentration in the process off-gas above the bed averaged 1.1%, with a maximum peak of 2.1%. The H_2S content was $\sim$1% of the SO_2 content in the process off-gas. The sulfur material balance, Fig. 14, has been calculated to be 96.1%.

One objective of cyclic combustion-regeneration experiments is to determine the extent of particle breakup (and elutriation from the fluidized bed) during regeneration. Breakup could result from attrition occurring in the fluidized bed or from chemical conversion of the compounds. During regeneration, calcium carbonate is decarbonated and $CaSO_4$ is converted to CaO (or CaS).

The particle-size distribution data (shown in Table 13) for the sulfated Tymochtee dolomite feed material, the primary cyclone product, and the combined final bed and overflow products indicate that decrepitation occurred during the regeneration step. The feed material, with a mean particle diameter of 772 μm, had less than 6% of -45 mesh solids. Material elutriated from the fluidized bed and collected in the cyclone had a lower mean particle diameter of 292 μm and considerably more of -45 mesh solids (58.5% of the total).

The distribution data for the primary-cyclone solids show that about 40% of the solids collected in the cyclone were in the -25 to +45 mesh range. Particles in this size range would not be expected to

---

[*] The concentration of the off-gas constituents exiting the bed are calculated values. In regeneration experiments with continuous additive feed, gas leaving the fluidized bed is diluted with additive transport gas and the concentrations of the off-gas constituents are measured after the combined gases leave the regenerator. The concentration of a particular off-gas constituent above the bed is then calculated by multiplying its concentrations in the diluted stream by the ratio of the flow rates in the diluted and undiluted streams.

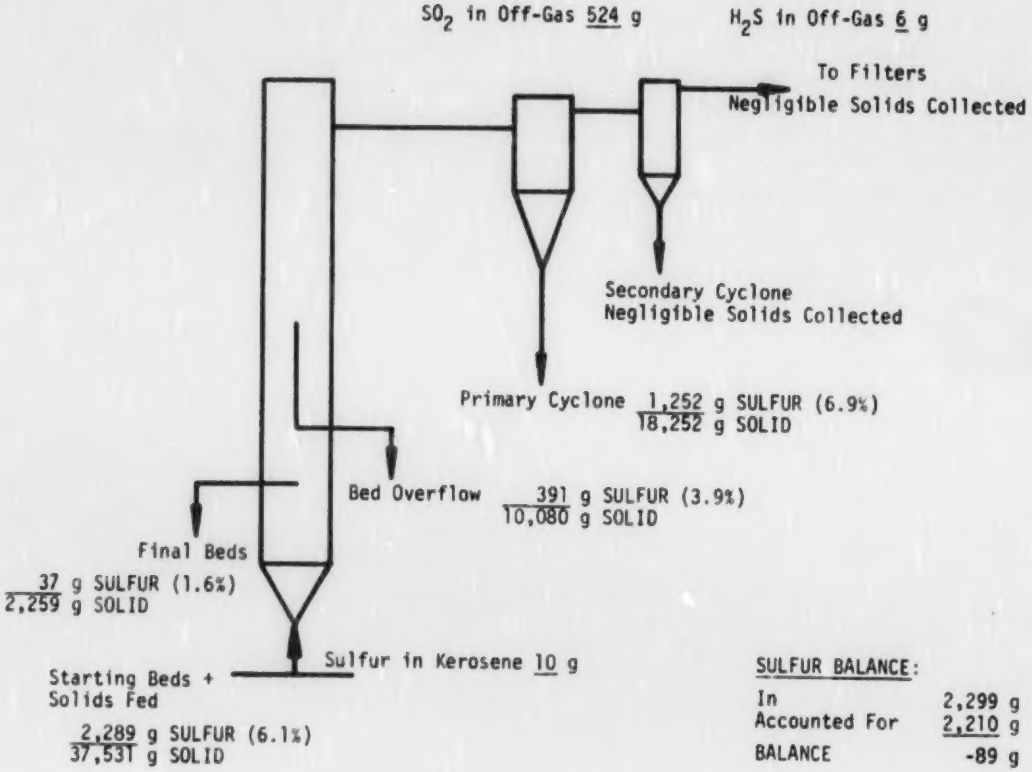

SO2 in Off-Gas 524 g
H2S in Off-Gas 6 g
To Filters
Negligible Solids Collected
Secondary Cyclone
Negligible Solids Collected
Primary Cyclone 1,252 g SULFUR (6.9%)
18,252 g SOLID
Bed Overflow 391 g SULFUR (3.9%)
10,080 g SOLID
Final Beds
37 g SULFUR (1.6%)
2,259 g SOLID
Sulfur in Kerosene 10 g
Starting Beds + Solids Fed
2,289 g SULFUR (6.1%)
37,531 g SOLID
SULFUR BALANCE:
In 2,299 g
Accounted For 2,210 g
BALANCE -89 g

Fig. 14. Sulfur Distribution in Regeneration Experiment REDUC-12

elutriate at the 3.0 ft/sec gas velocity in the bed. However, the gas velocity is higher than 3.0 ft/sec in the upper zone of the regenerator. This higher gas velocity results from the fact that the gas which pneumatically conveys the additive solids to the regenerator (through a line that enters the top of the regenerator and terminates about a foot above the bed) and the fluidizing-gas streams meet in the upper zone of the regenerator and exit together. The gas velocity of the combined streams above this meeting point may be as high as 6 ft/sec. Solids that may slug from the bed into the upper zone of the regenerator could be carried out of the regenerator by the higher gas velocity. A better system, either terminating the carrier gas line at the top of the regenerator or removing the feed solids in the carrier gas by a cyclone external to the regenerator and then feeding the solids to the bed via a dipleg, is being considered.

Table 13. Comparative Particle-Size Distributions of Materials Fed and Removed from Experiment REDUC-12

U. S. Sieve Sizes	Starting Bed and Feed Material (wt %)	Primary Cyclone (wt %)	Composite Final Bed and Overflow (wt %)
+ 14	0.54	0.00	0.65
-14 + 25	45.77	0.00	33.23
-25 + 35	32.65	10.22	41.79
-35 + 45	15.22	31.56	16.99
-45 + 80	5.82	28.44	6.22
-80 + 170	0.00	8.87	0.84
- 170	0.00	20.92	0.29
Mean Particle Dia (μm)	772	292	706

Because of weight changes that occur in the solids through the chemical reactions, the percentage of feed solids elutriated from the regenerator cannot be determined from weight data for solids input and output. However, calcium material balance data indicate that about 55% of the solids fed to the regenerator were elutriated from the regenerator in this experiment.

The chemical composition of the feed to the regenerator, the product solids removed from the regenerator, and the solids removed from the first cyclone are shown in Table 14. Very little sulfide (0.06 wt %) was found in the regenerator product. The regenerator feed and product streams contained 25.9 and 13.3 wt % $CaSO_4$, respectively.

Table 14. Chemical Composition of Solids in Exp. REDUC-12

	$CaSO_4$ (wt %)	CaS (wt %)	CaO (wt %)
Feed to Regenerator	25.9		
Product from Regenerator	13.3	0.06	32.7
First Cyclone	27.6	1.20	25.9

5. Regeneration by the Reaction, $CaSO_4 + CO \rightarrow CaCO_3 + SO_2$

The one-step reductive regeneration process is generally conducted at a high temperature (1900-2000°F) to reduce the sulfated additive to CaO and liberate SO_2. However, the results of experiment REDUC-8 led to consideration of conducting the reductive regeneration process at lower temperatures so as to yield $CaCO_3$ (rather than CaO) and SO_2. One potential advantage of a lower-temperature one-step reductive regeneration process is less rapid deactivation of the sorbent than that which occurs in the higher-temperature one-step process.

The $CaSO_4$ resulting from the sulfation of dolomite or limestone in the combustor could, if the kinetics are favorable, be regenerated by the reaction

$$CaSO_4 + CO \rightleftarrows CaCO_3 + SO_2$$

Equilibrium SO_2 concentrations are relatively high at low temperatures. For example, with a 5% CO concentration and a temperature of 1700°F, the equilibrium SO_2 concentration is ~6.5%. The ~4% peak concentrations at 1600-1700°F obtained in the 2-in.-dia laboratory-scale regeneration experiments described below may have resulted because conditions were suitable for this reaction to occur (see data in Appendix C).

A competing reaction

$$1/4\ CaSO_4 + CO \rightarrow 1/4\ CaS + CO_2$$

must be avoided by operating at a high CO_2/CO ratio and a low temperature and with O_2 present to reconvert CaS to $CaSO_4$. To avoid decomposing $CaCO_3$, the partial pressure of CO_2 must be 0.8 to 1.8 atm at 1600°F and 1700°F, respectively.

Operating conditions and results for a single experiment (REDUC-13) completed in the 3-in.-dia regenerator are presented in Table 15 (see also Tables 11a and 11b). The experiment was made at a system pressure of 2.8 atm absolute. A CO_2 partial pressure of 2.4 atm was maintained, sufficient to keep the carbonate from decomposing at a temperature of ~1730°F. The $CaSO_4$ (Drierite) was fed continuously into the bed at a rate of 6 lb/hr. The starting bed was five pounds of $CaSO_4$. The temperature of the fluidized bed varied during the experiment and the resulting data are only partially indicative of the results that might be obtained if steady state had been achieved. A stable bed temperature of 1650°F was desired but lower temperatures mainly prevailed.

The measured SO_2 concentrations in the process off-gas were considerably less than the equilibrium concentrations. Concentrations of SO_2 never exceeded 0.2% during the experiment, whereas equilibrium concentrations at the process conditions range from 3 to 6% SO_2. About 15% of the sulfur content in the off-gas was H_2S. Very little sulfur as sulfide was present in samples removed from the product (which continuously overflowed from the bed) and from the final bed. The final bed contained 20.5 wt % total sulfur and 0.25 wt % sulfide and the overflow product contained 21.5 wt % total sulfur and 0.07 wt % sulfide. Only ~70% of the sulfur was accounted for and ~12% total regeneration of the $CaSO_4$ was achieved.

Table 15. Operating Conditions and Results for Experiment REDUC-13

Equipment:	ANL 3-in.-dia, fluidized-bed regenerator
Feed Material:	$CaSO_4$ (Drierite)
Feed Rate:	6 lb/hr
Starting Bed:	$CaSO_4$ (Drierite)
System Pressure:	2.8 atm absolute

Bed Temp (°F)	Gas Velocity (ft/sec)	Input Flow Rates[a]				Off-Gas Concentrations				Avg. SO_2 Conc. (vol %)
		O_2 (cfm)	Kerosene (cc/min)	N_2 (cfm)	CO_2 (cfm)	O_2 (vol %)	CO (vol %)	NO (ppm)	CH_4 (vol %)	
1724	2.4	0.6	23.3	1.0	3.9	1.8	5.2	274	1.4	0.14
1500	2.7	0.4	29.3	1.0	5.0	1.5	4.3	610	2.0	0.15
1455	2.4	0.4	23.3	0.8	5.0	1.4	4.3	620	2.0	0.11

[a] All gas flows at 70°F and 1 atm.

6. Kerosene Combustion Products

In the final two regeneration experiments conducted in the 3-in.-dia regenerator, the partial combustion of kerosene was the sole source of the reducing gases used for the reduction of $CaSO_4$. To obtain data on the species and concentrations of gases at different temperatures and kerosene/oxygen ratios, kerosene was partially combusted in a fluidized bed of alumina (Al_2O_3). Nitrogen at 2.5 cfm (70°F, 1 atm) was the diluent gas. Gas velocity ranged from 2.1 to 2.8 ft/sec, and the system pressure was ∿25 psia. Bed temperatures ranged from 1600°F to 1900°F and kerosene/oxygen ratios from 16 to 27 cc kerosene/ft^3 oxygen.

Data were obtained during 8 steady-state periods and showed that the CO and CH_4 concentrations in the off-gas varied directly with the kerosene/oxygen ratios. Analysis of components other than CO and CH_4 in an off-gas sample, taken when the temperature of the fluidized bed was 1890°F and the kerosene/oxygen ratio was 25.9 cc kerosene/cfm O_2, showed that

a) the ethylene concentration was 0.15%,

b) the ethane concentration was less than 0.05%,

c) the hydrogen concentration was ∿9%.

An additional and similar experiment will be made to obtain more data so that CH_4 and CO concentrations in the off-gas can be correlated with dependent variables of bed temperature and kerosene/oxygen ratio.

IV. LABORATORY-SCALE REGENERATION STUDIES

A. Introduction and Review of Previous Work

Data have been obtained in the 2-in.-dia, batch, fluidized-bed reactor on two regeneration processes under consideration. These processes are as follows:

1. Reductive decomposition of calcium sulfate.
2. Reduction of calcium sulfate to calcium sulfide followed by reaction of calcium sulfide with carbon dioxide and steam.

A preliminary investigation has also been made of a third scheme in which $CaSO_4$ is reacted with H_2 and CO_2 at a temperature below 1400°F. In any practical application of these processes, the sulfur-containing gas produced in the reaction would be treated further to make elemental sulfur.

During the previous year, the thermodynamics of the above processes were studied.[1] The yields of sulfur-containing gases and the compositions of solid phases were calculated. The variations of these yields and compositions with temperature, pressure, and gas composition for a system at equilibrium were also calculated.

Also, in previous studies of the reductive decomposition process, experiments were performed in a static system to test the accuracy of the equilibrium compositions calculated for the reduction of $CaSO_4$ with CO/CO_2 mixtures. In most cases, good agreement was obtained between experimental and calculated values for SO_2 levels when $CaSO_4$ was reacted with CO/CO_2 over a range of ratios.

Previous developments in the two-step process have shown that:

1. Complete reduction of $CaSO_4$ to CaS can be achieved at 1600°F with H_2 or CO as reductant.
2. Equilibrium concentrations of H_2S can be obtained when CaS is reacted with CO_2/H_2O gas mixtures at 1000-1200°F, but the sulfur removal is poor, generally 50% or less.
3. When cycling solids through several sulfation-reduction-regeneration steps (the product of the second step was resulfated with SO_2-containing gas), the peak concentrations of H_2S decrease and less of the total sulfur is released as the cycling continues.

B. Equipment

The experiments were performed in batch, fluidized-bed reactors: CATS-34 and CATS-35 in a 1-in.-dia alumina tube reactor and all other experiments in a 2-in.-dia stainless steel reactor. A schematic of the 2-in. reactor system is presented in Fig. 15. Except for the reactor, the system is the same for the 1-in.-dia reactor. The pressure of the system is controlled by a pressure transmitter, pneumatic controller, and a pneumatic valve. Temperature in the reactor is controlled by adjusting the amperage in the resistance heaters around the reactor. Analysis of the effluent gas is performed with infrared analyzers, a gas chromatograph, and a quadrupole mass spectrometer.

C. Materials

The bed material consists of either $CaSO_4$ (Drierite) or partially sulfated dolomite or limestone obtained from the combustion of coal in the additive. Nitrogen and carbon dioxide are obtained from the evaporation of the liquids or from normal cylinder sources. The other reactant gases were obtained from normal cylinder sources.

D. Results and Discussion

1. Two-Step Process

Development studies of the two-step process have included (1) cyclic experiments in which CaO was sulfided with H_2S, and the CaS reconverted to $CaCO_3$ with H_2O/CO_2 to determine if the absence of $CaSO_4$ (which had been present in previous cyclic experiments) affected the release of sulfur, (2) scouting experiments on the effect of higher regeneration temperature on sulfur release, the use of limestone (instead of dolomite), and the catalytic reduction of $CaSO_4$ by iron, (3) the assessment of two-stage, two-step regeneration process, and (4) examination of particles from the cyclic experiments.

a. Cyclic Sulfiding-Regeneration Experiments. To determine whether the removal of sulfur is inhibited by undesirable side reactions between the components of the system ($CaSO_4$, CaS, and $CaCO_3$), experiments were performed to convert CaS to $CaCO_3$ with sulfate phase absent. Data obtained previously in the cyclic experiments including sulfation had shown that much sulfur was not being released from the particle during the regeneration step and that sorbent activity fell substantially upon cycling.

Experiment CATS-22 consisted of three cycles using dolomite. Each cycle comprised calcination of the $MgCO_3$ fraction of the dolomite to MgO, conversion of $CaCO_3$ to CaS with H_2S, and regeneration of CaS to $CaCO_3$ with CO_2/H_2O. Data for the inlet gas composition, temperature, reaction time, and final bed composition

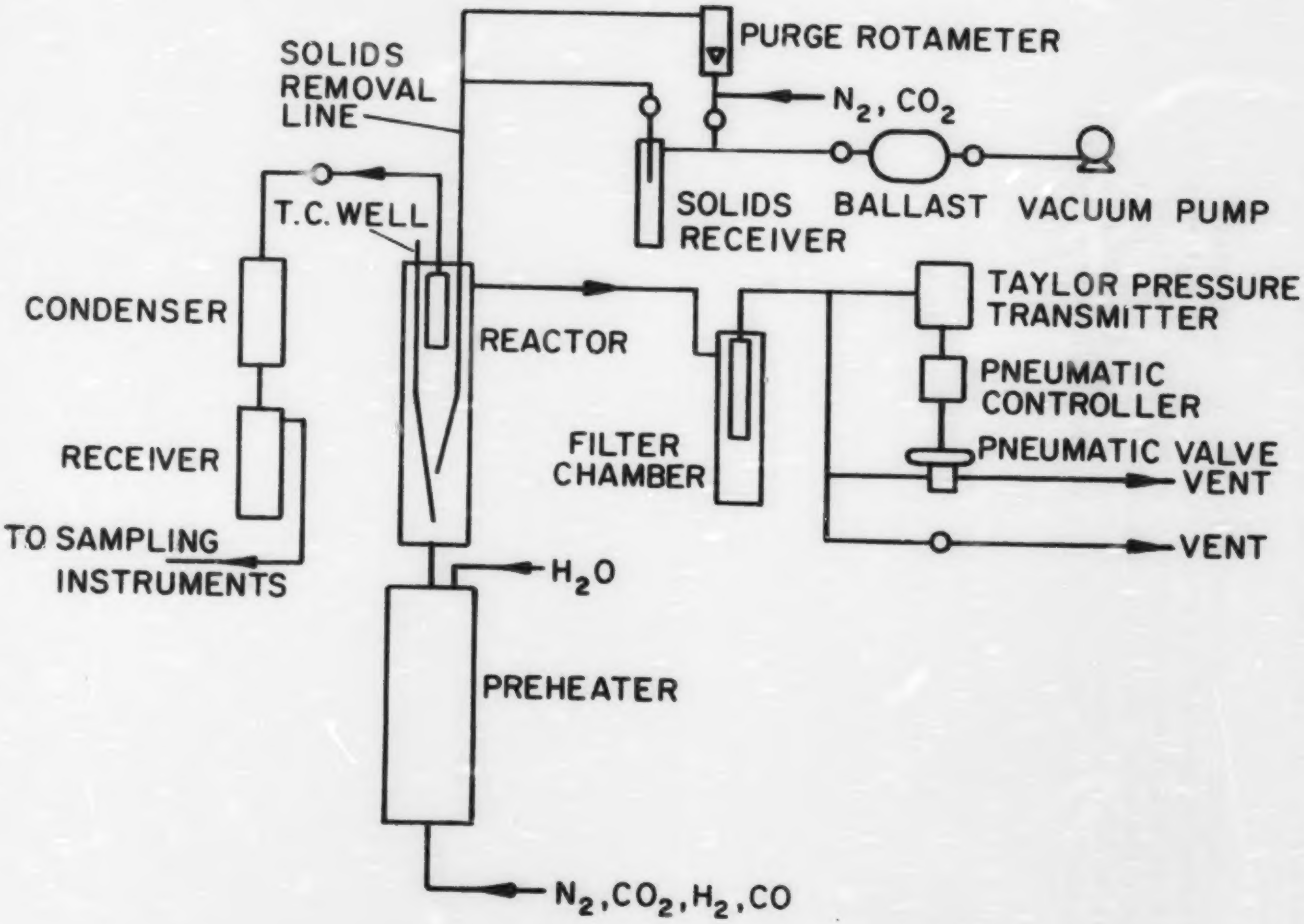

SOLIDS REMOVAL LINE
PURGE ROTAMETER
N_2, CO_2
T.C. WELL
SOLIDS RECEIVER
BALLAST
VACUUM PUMP
CONDENSER
REACTOR
TAYLOR PRESSURE TRANSMITTER
PNEUMATIC CONTROLLER
PNEUMATIC VALVE
VENT
RECEIVER
FILTER CHAMBER
VENT
TO SAMPLING INSTRUMENTS
H_2O
PREHEATER
N_2,CO_2,H_2,CO

Fig. 15. Two-in.-Dia, Fluidized-Bed Reactor System

are presented in Table 16. Data for the H_2S concentration in the effluent gas stream during regeneration are presented in Fig. 15. The regeneration step was terminated when the H_2S release appeared to stop.

The data indicate that after the sulfiding steps the sulfur content of the bed was essentially in the form of sulfide; therefore, any effect of sulfate interfering with the removal of sulfur may be neglected. After the regeneration step in cycles 1, 2, and 3, the sulfide concentrations in the bed were 6.5, 13.7, and 13.2 wt %, respectively. Less sulfur was removed as H_2S in succeeding cycles.

Table 16. Conditions and Results for H_2S Addition and Regeneration Steps of Experiment CATS-22

Initial Bed: 1 kg dolomite No. 1337

(Bed half-calcined at 1500°F with 40% CO_2-60% N_2 before each cycle.)

H_2S Addition

Cycle No.	Inlet-Gas[a] Flow Rates			Temp (°F)	Reaction Time (min)	Pressure (atm)	Sulfur Conc. in Final Bed	
	CO_2 (cfm)	N_2 (cfm)	H_2S (cfm)				Total S (wt %)	$S^=$ (wt %)
1	0.27	0.62	3.3	1500	60	2.8	-	-
2	0.39	0.33	2.6	1500	50	2.7	21.3	21.1
3	0.35	0.41	2.2	1500	32	1.9	17.4	16.7

Regeneration

Cycle No.	Inlet-Gas[a] Flow Rates		Gas Velocity (ft/sec)	Approx. Temp (°F)	Reaction Time (min)	Pressure (atm)	Sulfur Conc. in Final Bed	
	CO_2 (cfm)	H_2O (cfm)					Total S (wt %)	$S^=$ (wt %)
1	0.88	0.88	1.3	1100	60	10	7.2	6.5
2	0.88	0.88	1.3	1100	35	10	14.3	13.7
3	0.88	0.88	1.3	1100	25	10	14.1	13.2

[a] All Gas flows at 1 atm and 70°F.

The peak H_2S concentrations in the effluent gas steam during regeneration of CaS to $CaCO_3$ in cycles 1, 2, and 3 were 26.5, 14, and 12.7 vol % (dry basis) (see Fig. 16). The calculated equilibrium concentration at 1100°F is ~21 vol % (dry basis). The duration of the regeneration reaction decreased from 58 min for the first regeneration to 25 min for the third regeneration. These results indicate that the amount of sulfur removal decreased with each succeeding regeneration as it had when sulfate was present in earlier cyclic experiments.[1] It appears that the problem of sulfur removal cannot be attributed to interference due to the presence of $CaSO_4$ in the bed.

A particle-size analysis (Table 17) was performed on initial and final bed material and on fines elutriated into the filter chamber. The results indicate that substantial attrition of bed particles occurred during the cycles.

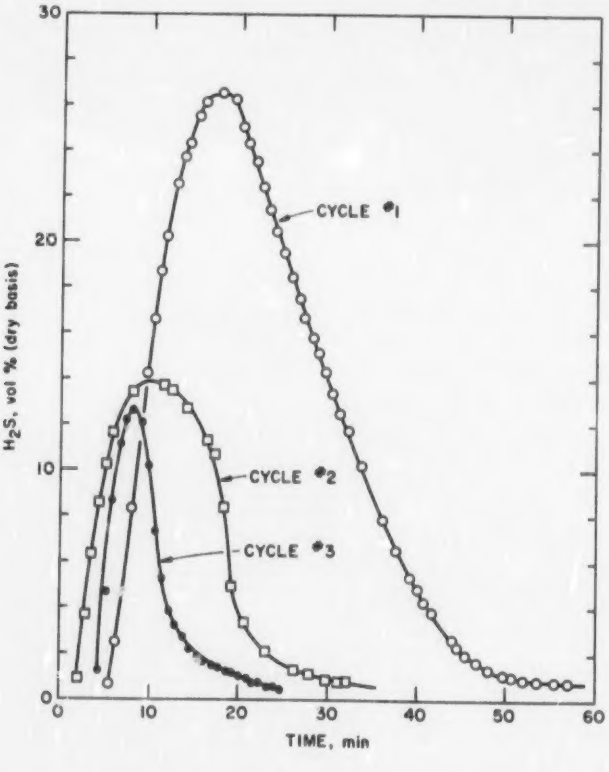


Fig. 16. H_2S Concentration in Effluent-Gas Stream during Regeneration Step of Experiment CATS-22

Table 17. Screen Analysis of Initial and Final Bed Material and Fines for Experiment CATS-22

U.S. Sieve No.	Sieve Analysis (wt %) Initial Bed Dolomite No. 1337	Final Bed	Fines
+ 25	6.7	6.0	
-25 + 40	49.3	31.3	0.5
-40 + 60	20.2	26.6	0.5
-60 + 80	16.6	15.6	0.9
-80 +100	4.9	9.6	4.3
-100 +230	1.8	8.3	58.3
-230	0.4	2.6	35.5
	Total wt, g	384	222
	S content, wt %	14.1	6.2
	Weight of S, g	53.3	13.8

Experiment CATS-23 was performed to determine whether a low conversion of $CaCO_3$ to CaS and the addition of a reductant (H_2) to the regenerating gas mixture would affect the removal of sulfur from the bed. Two cycles were performed at the operating conditions and with the results shown in Table 18.

Table 18. Conditions and Results for H_2S Addition and Regeneration Steps of Experiment CATS-23

Initial Bed: 1 kg dolomite No. 1337

(Bed half-calcined before each cycle at 1500°F with 40% CO_2-60% N_2.)

H_2S Addition

Cycle No.	Inlet-Gas[a] Flow Rates CO_2 (cfm)	N_2 (cfm)	H_2S (cfh)	Temp (°F)	Reaction Time (min)	Pressure (atm)	Sulfur Conc. in Final Bed (wt %)
1	0.19	0.26	1.3	1500	40	1.3	5.8
2	0.19	0.26	1.3	1500	40	1.3	6.5

Regeneration

Cycle No.	Inlet-Gas[a] Flow Rates CO_2 (cfm)	H_2O (cfm)	H_2 (cfm)	Temp (°F)	Reaction Time (min)	Pressure (atm)	Sulfur Conc. in Final Bed (wt %)
1	0.88	0.88	0.18	1100	78	10	2.9
2	0.88	0.88	0.18	1100	68	10	5.1

[a] All gas flows at 1 atm and 70°F.

The sulfur content of the bed decreased from 5.8 wt % after the first H_2S addition to 2.9 wt % after the first regeneration step, and from 6.5 wt % to 5.1 wt % in the second cycle. The peak H_2S concentrations in the effluent gas (Fig. 17) were 16.1 vol % and 13.9 vol % (dry basis) for cycles 1 and 2, respectively. Much less sulfur was released in the second cycle, which has been typical in all of the cyclic experiments, and it was concluded that neither low conversion of $CaCO_3$ to CaS nor the presence of hydrogen would significantly help the problem of sulfur release during cycling.

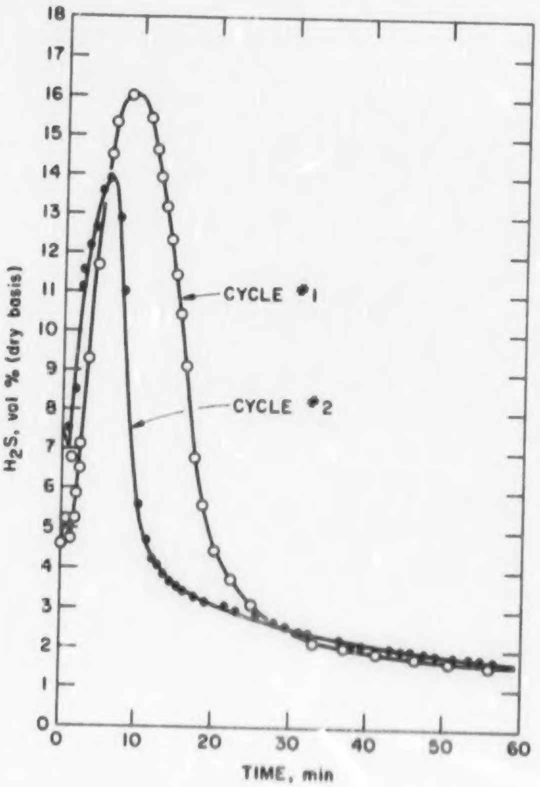


Fig. 17. H_2S Concentration in Effluent-Gas Stream during Regeneration Step of Experiment CATS-23

b. Effect of Higher Regeneration Temperatures on Sulfur Release from the Particle. Earlier attempts to convert $CaSO_4$ to $CaCO_3$ yielded a product that probably contained too much sulfur for reuse as additive. In this earlier work, conversion of CaS to $CaCO_3$ was performed at 1000°F or 1100°F to take advantage of high equilibrium concentrations of H_2S (37 and 20 vol %, dry basis, respectively) in the gas phase.

To determine if reaction of CaS and CO_2/H_2O at a higher temperature would increase the removal of sulfur, a laboratory-scale experiment was performed in which CaS was converted to $CaCO_3$ at 1250°F (at this temperature the equilibrium concentration of H_2S is ~8 vol %, dry basis). Gas compositions, temperatures, reaction time, and bed compositions for this experiment (CATS-24) are presented in Table 19.

Table 19. Conditions and Results for H_2S Addition and Regeneration Steps of Experiment CATS-24

Initial Bed: 1 kg dolomite No. 1337

(Bed half-calcined at 1500°F with 40% CO_2-60% N_2 at 1 atm.)

H_2S Addition

Inlet-Gas[a] Flow Rates							
CO_2 (cfm)	N_2 (cfm)	H_2S (cfm)	H_2 (cfm)	Temp (°F)	Reaction Time (min)	Pressure (atm)	Sulfur Conc. in Bed at End of Step (wt %)
0.24	0.33	0.027	0.04	1500	40	2.1	6.16

Regeneration

Inlet-Gas[a] Flow Rates						
CO_2 (cfm)	H_2O (cfm)	H_2 (cfm)	Temp (°F)	Reaction Time (min)	Pressure (atm)	Sulfur Conc. in Final Bed (wt %)
0.88	0.88	0.18	1250	40	10	2.45

[a] Gas flow rates at 70°F and 1 atm.

Data for the H_2S content during the run are presented in Fig. 18. The peak concentration of H_2S in the effluent gas stream was 5.9 vol % (dry basis). As was previously noted, the equilibrium concentration of H_2S expected at 1250°F is ~8 vol % (dry basis).

After completion of the reaction, a sample of the bed was obtained and analyzed for sulfur content. The data indicate that the sulfur content of the bed decreased from 6.2 wt % at the end of the H_2S addition step to 2.5 wt % at the end of the regeneration step. In the first cycle of an earlier experiment (CATS-23, reported above) that was identical to CATS-24, except that the regeneration step was performed at 1100°F instead of 1250°F, the sulfur concentrations

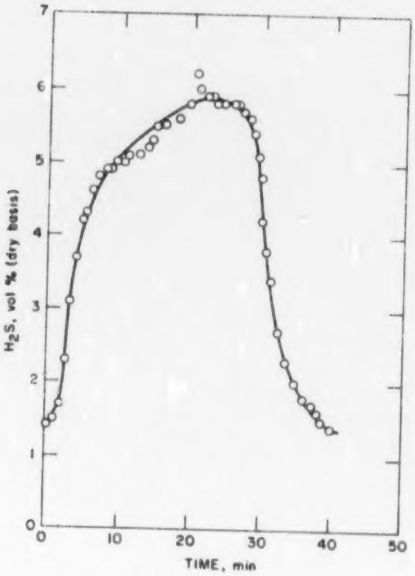


Fig. 18. H_2S Concentration in Effluent-Gas Stream during Regeneration Step of Experiment CATS-24

in the bed before and after the regeneration step for cycle 1 were 5.8 wt % and 2.9 wt %, respectively. These data indicate that sulfur removal can be moderately increased by increasing the regeneration temperature to 1250°F.

c. Regeneration of Limestone. To determine the effect of additive composition on the removal of sulfur, a laboratory-scale experiment (CATS-26) was performed in which limestone instead of dolomite was used as the additive. Inlet-gas compositions, temperatures, reaction times, and bed compositions for the two cycles of the experiment are presented in Table 20.

In the sulfiding step of cycle 1, breakthrough of H_2S (*i.e.*, when H_2S was first detected in the off-gas) occurred after 30 min of reaction time. Conversion of 12.5% of the $CaCO_3$ to CaS was obtained. In cycle 2, H_2S breakthrough was indicated after 45 min of reaction time, and 25% of the $CaCO_3$ remaining in the bed after cycle 1 was converted to CaS. Peak concentrations during regeneration of 5.3 vol % (dry basis) and 5.8 vol % (dry basis) H_2S were obtained in cycles 1 and 2, respectively (see Fig. 19). The equilibrium H_2S concentration expected at 1250°F for the reaction is ∿8 vol % (dry basis).

In cycle 1, the sulfur content of the bed decreased from 6.7 wt % before regeneration to 5.2 wt % after the conversion. The sulfur content, 10.8 wt %, did not change during the regeneration step of cycle 2. In a previous experiment (CATS-24) with reaction

Table 20. Conditions and Results for H_2S Addition and Regeneration Steps of Experiment CATS-26

Initial Bed: 1 kg limestone No. 1359

Equipment: 2-in.-dia, fluidized-bed reactor

H_2S Addition

Cycle No.	Inlet-Gas[a] Flow Rates				Temp (°F)	Reaction Time (min)	Pressure (atm)	Sulfur Conc. in Bed at End of Step (wt %)
	CO_2 (cfm)	N_2 (cfm)	H_2S (cfm)	H_2 (cfm)				
1	0.23	0.28	0.03	0.027	1500	30	2	6.7
2	0.23	0.28	0.03	0.027	1500	45	2	10.8

Regeneration

Cycle No.	Inlet-Gas[a] Flow Rates			Temp (°F)	Reaction Time (min)	Pressure (atm)	Sulfur Conc. in Final Bed (wt %)
	CO_2 (cfm)	H_2O (cfm)	H_2 (cfm)				
1	0.26	0.26	0.18	1250	30	10	5.2
2	0.26	0.26	0.00	1250	40	10	10.8

[a] Gas Flow Rates at 70°F and 1 atm.

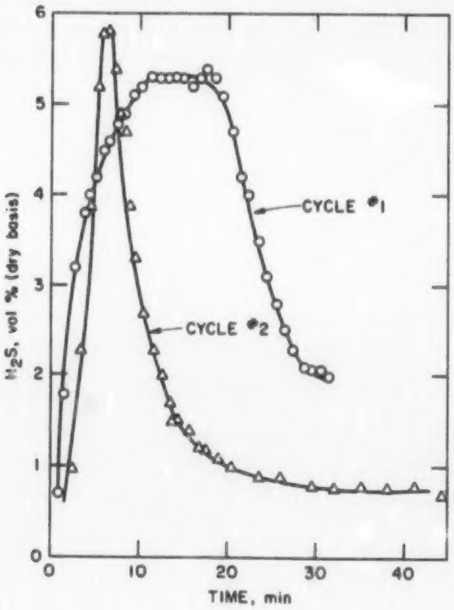


Fig. 19. H_2S Concentration in Effluent-Gas Stream during Regeneration Step of Experiment CATS-26

conditions identical to cycle 1 except that partially calcined dolomite was the bed material, the sulfur content decreased from 6.2 wt % to 2.4 wt % upon regeneration in cycle 1. These data indicate that, at these experimental conditions, the composition of the additive has an effect on the removal of sulfur and that dolomite is a better choice as an additive than is limestone. It should be noted that limestone is not decarbonated (calcined) at the experimental conditions whereas the dolomite is half calcined. Calcination probably increased the particle surface area of the dolomite.

d. Effect of Presence of Hydrogen during Second Step on Sulfur Release. Experiment CATS-28 was performed to determine whether the presence of hydrogen during both steps of the process prevents the suspected formation of intermediates such as calcium polysulfides (which may interfere with the regeneration of sulfated dolomite). The bed material, consisting of 0.5 kg of partially sulfated dolomite (containing 15.4 wt % S), was reduced at 1600°F with 25 vol % H_2-37.5 vol % CO_2-37.5 vol % N_2 at 10 atm for 5.5 hr to convert the $CaSO_4$ to CaS. Process conditions for the reduction step are presented in Table 21. The sulfur and sulfide concentrations of the bed material after reduction were 18.9 wt % and 19.1 wt %, respectively, indicating that conversion of sulfate to sulfide was complete. The bed, now consisting of CaS, $CaCO_3$, and MgO, was reacted at 1200-1400°F with 17 vol % H_2-41.5 vol % CO_2-41.5 vol % H_2O at 10 atm for 52 min. The process conditions for the regeneration step are also presented in Table 21.

Table 21. Process Conditions and Bed Compositions for Experiment CATS-28

Bed Material: 0.5 kg partially sulfated dolomite (15.4 wt % S)

Reduction Step

Temp (°F)	Pressure (atm)	Time (hr)	Inlet-Gas[a] Flow Rates			Sulfur Conc. in Bed at End of Step	
			CO_2 (cfm)	N_2 (cfm)	H_2 (cfm)	Total S (wt %)	$S^=$ (wt %)
1600	10	5.5	1	1	0.7	18.9	19.1

Regeneration Step

Temp (°F)	Pressure (atm)	Time (min)	Inlet-Gas[a] Flow Rates			Sulfur Conc. in Final Bed	
			CO_2 (cfm)	H_2O (cfm)	H_2 (cfm)	Total S (wt %)	$S^=$ (wt %)
1200	10	0-27	1.3	1.3	0.5		
1400	10	27-42	1.3	1.3	0.5		
1200	10	42-52	1.3	1.3	0.5	16.3	16.8

[a] Gas Flow Rates at 70°F and 1 atm.

A portion of the effluent gas stream was monitored for H_2S content. The H_2S content of the effluent gas stream was ∿0.3 vol % (dry basis) during the first 27 min at 1200°F. When the temperature was increased to 1400°F, the H_2S content of the effluent increased to 1.2 vol % (dry basis) in 6 min, then decreased slowly to 0.8 vol % (dry basis) after a total of 15 min at 1400°F. The temperature was lowered to 1200°F, and the H_2S content of the effluent gas decreased to ∿0.3 vol % (dry basis) and remained constant at that concentration for 10 min. The equilibrium concentrations of H_2S expected for this reaction at 1200°F and 1400°F are ∿5 vol % (dry basis) and 1.5 vol % (dry basis). These results indicate that at low temperatures, where the equilibrium concentration of H_2S is favorable, the kinetics of the reaction are not rapid enough for equilibrium to be established in the system.

The sulfur and sulfide concentrations of the bed material after regeneration were 16.3 and 16.8 wt %, respectively, indicating that 12% of the sulfur had been removed. These results indicate that the presence of hydrogen during regeneration does not yield satisfactory sulfur removal.

e. Reduction of $CaSO_4$ Using CO and a Catalyst. It has been reported[2] that the reduction of calcium sulfate to calcium sulfide with CO as reductant is catalyzed by the addition of Fe_2O_3 to the bed, and that in one experiment a conversion of 97% occurred at 1250°F after 45 min. Experiment CATS-29 was made in an effort to confirm these results. In CATS-29, a bed of partially sulfated dolomite (9 wt % S) was mixed by tumbling with 10% by weight of Fe_2O_3 powder and reacted with an equimolar mixture of CO-CO_2-N_2 at 1250°F and 1 atm for 4.5 hours. The conversion of $CaSO_4$ to CaS was only 16.3% which is considerably less than the 97% reported conversion. It appeared that the Fe_2O_3 did not effectively catalyze the conversion of $CaSO_4$ to CaS in the presence of sulfated dolomite at these conditions.

f. Two-Stage Reactor Concept. Results of experiments on the first step of the two-step regeneration process indicate that sulfur compounds are likely to be evolved in small amounts in the reduction step. Loss of these sulfur compounds would be undesirable. When the reduction is carried out at 1600°F with CO, a small quantity of SO_2 is evolved. When the reduction is performed with 100% H_2, small amounts of H_2S are evolved.

To preclude release of these gases to the atmosphere, it appears desirable to pass both the gas and the reduced solids cocurrently from the reduction reactor to the regeneration reactor. Fortunately, the effluent gas from the reductor can be utilized as a reactant in the regenerator. When CO is used as the reductant, a reaction product is CO_2, which is a component of the regeneration gas. Similarly, when H_2 is used as reductant, H_2O, which is another component of the regeneration gas, is produced. Reductant in moderate excess is not likely to interfere with the subsequent process step.

For cocurrent flow of gas and solids between the two stages, it may be convenient to carry out the two steps in a single vessel having two stages. Such a vessel is illustrated in Fig. 20. Solids are fed to the lower stage, where reduction occurs. Then gas and solids flow upward, through the restriction, to the upper stage where regeneration occurs. Water reactant is fed to the upper stage. Some or all of this water could be in liquid form to help reduce the bed temperature to the desired level. The gas velocities in the two stages would be slightly different, but this should have no important consequences.

A further modification and simplification of the overall regeneration, sulfur-recovery process may be possible. If the temperature of the reduction stage is increased, say to 1800°F, greater amounts of SO_2 will be present in the gas leaving the reduction stage. By proper adjustment of the stage temperatures, it may be possible to produce a regenerator off-gas containing a mole ratio of H_2S/SO_2 of two. This gas would then be cooled and fed to a Claus reactor for direct conversion to sulfur.

To simulate the reduction stage of the envisioned reactor, sulfated dolomite from a combustion experiment was reacted at 1850°F with 2% CO in CO_2 for 80 min, and with 0.25% CO in CO_2 for 40 additional minutes. After this treatment, the bed was reacted with an equimolar mixture of CO_2/H_2O at 1250°F for 17 min to simulate the second stage. The results for the first-stage tests (Table 22) indicate that during the reduction step, the ratio of CO to CO_2 in the effluent gas stream was greater than the ratio in the inlet gas, possibly because carbon in the bed was reacting with CO_2 to produce CO. As the effluent gas CO/CO_2 ratio increased or moved to the CO-rich side of the coexistence line for $CaSO_4$ and CaS, the SO_2 content of the effluent gas stream was greater than would be expected from equilibrium calculations, but was less than would be expected at the $CaS/CaSO_4$ coexistence line. (Pressure of SO_2 in equilibrium with CO/CO_2 mixtures and the $CaS/CaSO_4$ coexistence line as a function of temperature have been presented earlier.[1]) When the ratio of CO to CO_2 was close to the coexistence line, the SO_2 content of the effluent gas stream was as expected from equilibrium calculations.[1] For example, at 1710°F the SO_2 pressure in the effluent gas stream was 0.011 atm at a CO/CO_2 ratio of 0.023. For comparison, the predicted SO_2 pressure at a CO/CO_2 ratio of 0.023 and 1710°F is 0.015 atm. At the coexistence line, the SO_2 pressure would be $\sim$0.140 atm.

During the following step to convert CaS to $CaCO_3$, no H_2S was found in the effluent gas stream; possibly no CaS was present after the reaction with CO/CO_2. Previous successful reductions of $CaSO_4$ to CaS using CO as reductant were performed at 1500°F and 100% CO.[1] It is possible that in this experiment (CATS-27) the CO content was too low to effect much reduction of $CaSO_4$ to CaS.

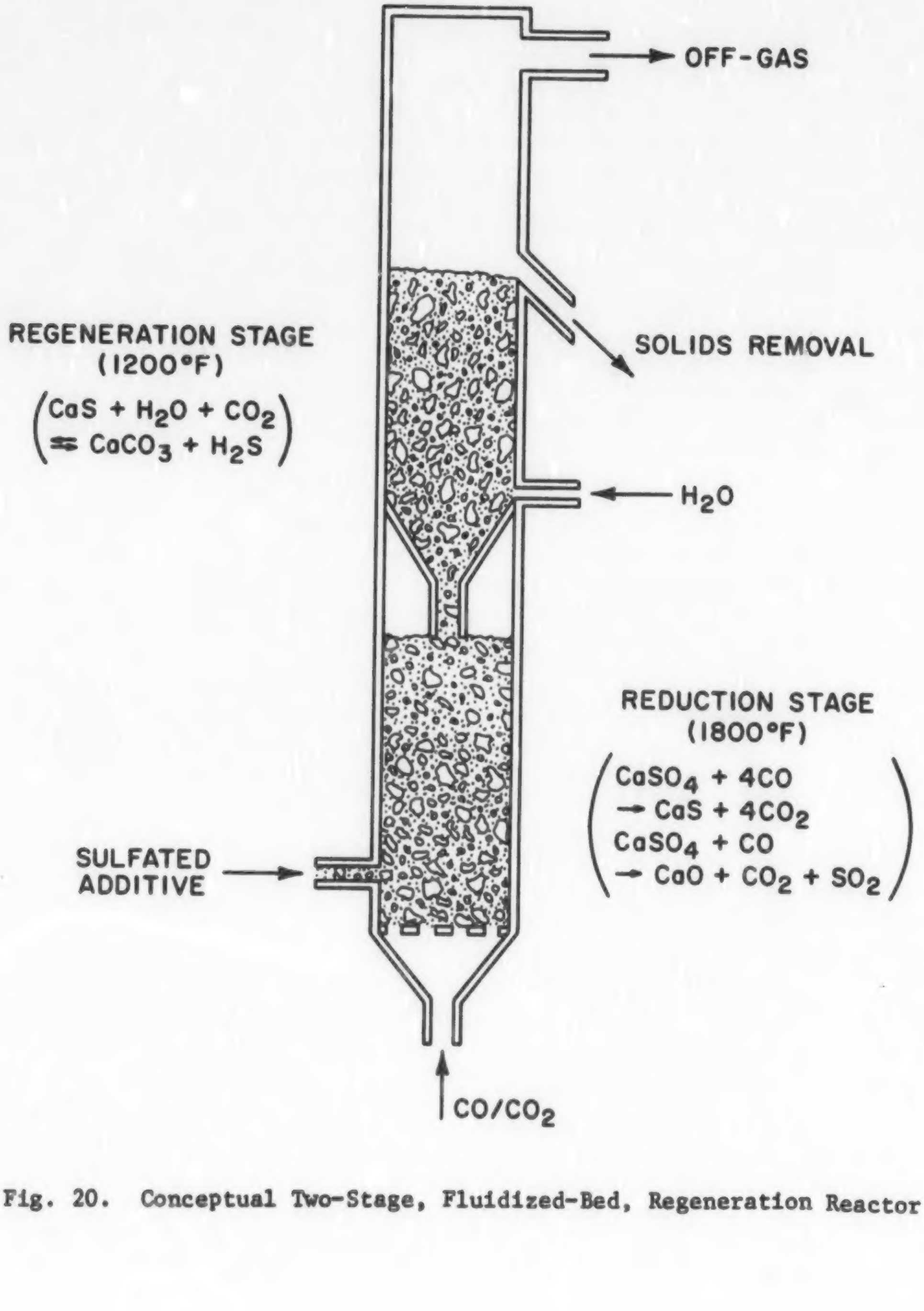

OFF-GAS
REGENERATION STAGE (1200°F)
(CaS + H2O + CO2 ⇌ CaCO3 + H2S)
SOLIDS REMOVAL
H2O
REDUCTION STAGE (1800°F)
(CaSO4 + 4CO → CaS + 4CO2
CaSO4 + CO → CaO + CO2 + SO2)
SULFATED ADDITIVE
CO/CO2

Fig. 20. Conceptual Two-Stage, Fluidized-Bed, Regeneration Reactor

Table 22. Composition of Effluent Gas Stream during Reaction of $CaSO_4$ with CO/CO_2 (Reduction Step) in Experiment CATS-27

Inlet-gas composition: 2% $CO-CO_2$, 0-80 min
0.25% $CO-CO_2$, 80-120 min

		Effluent Gas Stream			
Time (min)	Temp[a] (°F)	Ratio CO/CO_2	Pressure of SO_2 (atm)	Equilibrium Pressure of SO_2 at Exit CO/CO_2 Ratio and Bed Temperature (atm)	Approximate SO_2 Pressure on $CaS/CaSO_4$ Coexistence Line (atm)
10	1850	0.004	0.018	---	0.225
20	1840	0.036	0.069	0.015	0.215
30	1840	0.048	0.075	0.006	0.215
40	1840	0.059	0.061	0.004	0.215
50	1840	0.063	0.052	0.002	0.215
60	1835	0.065	0.043	0.002	0.210
70	1825	0.052	0.038	0.004	0.205
80	1810	0.032	0.027	0.015	0.195
90	1730	0.025	0.015	0.015	0.145
100	1710	0.023	0.011	0.015	0.140
110	1685	0.022	0.009	0.014	0.125
120	1665	0.022	0.008	0.011	0.115

[a] Temperature at middle of the bed.

Samples from different parts of the bed following the second step were analyzed for sulfur content. The bed had caked near the middle. The sulfur content in the upper third of the bed decreased from 3.7 wt % to 0.9 wt % during the reduction and regeneration steps. These results represent a sulfur removal which is better than the maximum sulfur removals of ∿50% obtained in previous two-step regeneration experiments.

g. Examination of Bed Particles from Sulfation-Regeneration Experiments in Fluidized-Bed Reactors. In earlier work, individual particles from the 2-in.-dia regenerator unit were examined by optical microscopy as part of an effort to clarify the mechanisms associated with sulfation, sulfiding, and regeneration.[1] In that work, a surface layer about 20 μm thick was observed on presumably sulfated dolomite particles in the 1-mm-dia size range.

The bed particles examined in current work were from (1) an earlier sulfation-regeneration experiment, in the 2-in.-dia unit, that consisted of six cycles with each cycle including sulfation and two-stage regeneration[1] and (2) sulfiding-regeneration experiments (CATS-22,

-23, -24, and -26) in which conversion of CaS to $CaCO_3$ was studied under various conditions. In the latter experiments, CaS was formed by reacting $CaCO_3$ with H_2S, rather than by the reduction of $CaSO_4$.

The techniques used to examine bed particles were optical microscopy, infrared spectroscopy, X-ray diffraction, and electron microprobe analysis. Initial examination was done with an optical microscope. Material obtained from the sulfation-regeneration experiment had a surface layer that was darker in color (brown-black) than the interior of the particles and was magnetic. Particles from experiments in which $CaSO_4$ was not formed (i.e., sulfiding-regeneration experiments) did not exhibit this surface layer. Starting material for the sulfation-regeneration experiments had been obtained from a combustion experiment carried out in the 6-in.-dia combustor. In all samples, the bulk structure of the particles appeared to consist of very small (0.3 μm) crystallites, as might be expected in calcined material. Because the size of the crystallites was below the resolving power of an optical microscope, reliable identification of the minerals and compounds present was not possible.

Therefore, a number of samples were examined by infrared spectroscopy to determine the presence of characteristic anions (e.g., carbonate and sulfate). Satisfactory results were obtained using both Nujor mulls and KBr pellets as matrix material.

X-ray diffraction patterns were obtained for a number of samples in order to identify the major minerals present. The X-ray results were in agreement with the infrared results.

The electron microprobe was used to examine a limited number of typical particles in order to establish the distribution of elements in the particles. Results of these examinations confirmed the presence of the surface layer that had been observed optically.

The IR spectroscopy, X-ray diffraction, and electron microprobe results were obtained on samples taken from the sulfation, reduction, and regeneration steps of cycle two in the sulfation-regeneration cyclic experiment, and from Experiment CATS-22. The infrared spectra are presented in Figs. 21 and 22, the microprobe data in Figs. 23 to 25, and the X-ray data in Table 23.

Material obtained from the second cycle sulfation step of the sulfation-regeneration experiment can be clearly seen to contain considerable sulfate ($SO_4^=$) by examination of Fig. 21a and Table 23. The infrared spectrum in Fig. 21a also indicates the presence of some residual carbonate ($CO_3^=$). The carbonate, however, was not detected by X-ray examination (Table 23). On the other hand, the X-ray data indicate some calcium sulfide (CaS) that was not identified by infrared (Figs. 21 and 22). Careful examination of the electron microprobe scan made on this material (Fig. 21) and on similar material (taken from the first sulfation step) shows that, in general, calcium and sulfur occur

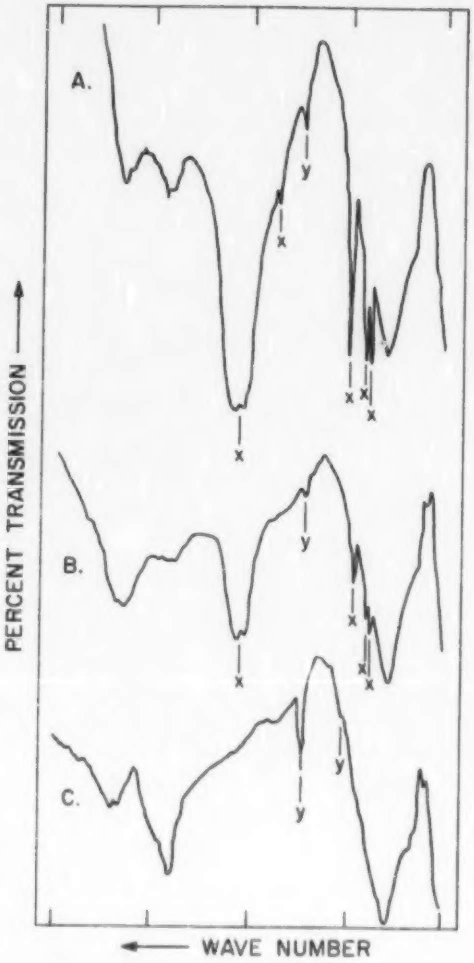


Fig. 21. Infrared Spectrum of Material Taken from Cycle Two of the Cyclic Sulfation-Regeneration Experiment: A. Material from Sulfation Step; B. Material from Reduction Step; C. Material from Regeneration Step

(x = Sulfate and y = Carbonate)

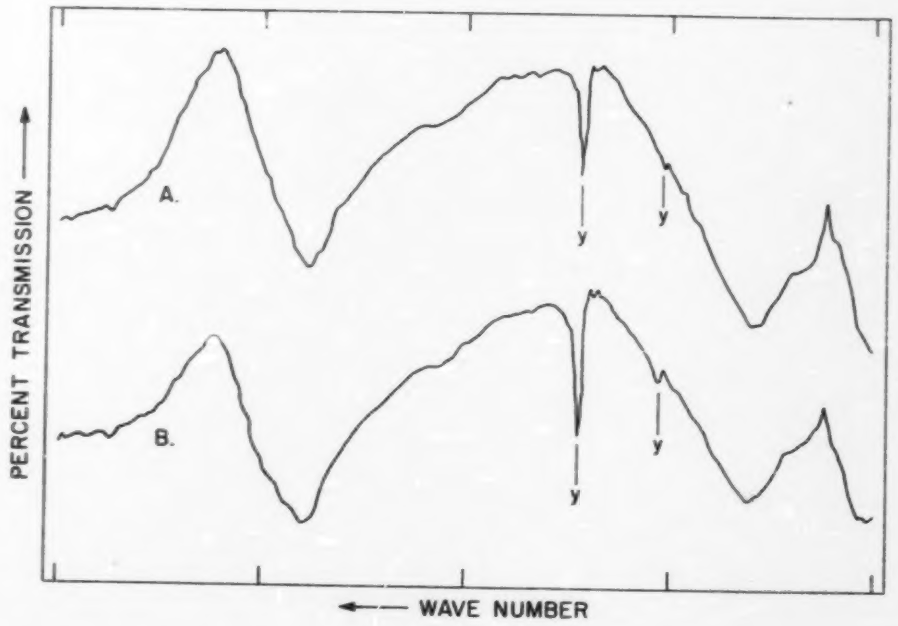


Fig. 22. Infrared Spectrum of Material Taken from Cycle Two of Experiment CATS-22: A. Material after Reaction with H_2S; B. Material after Regeneration Step

(y = Carbonate)

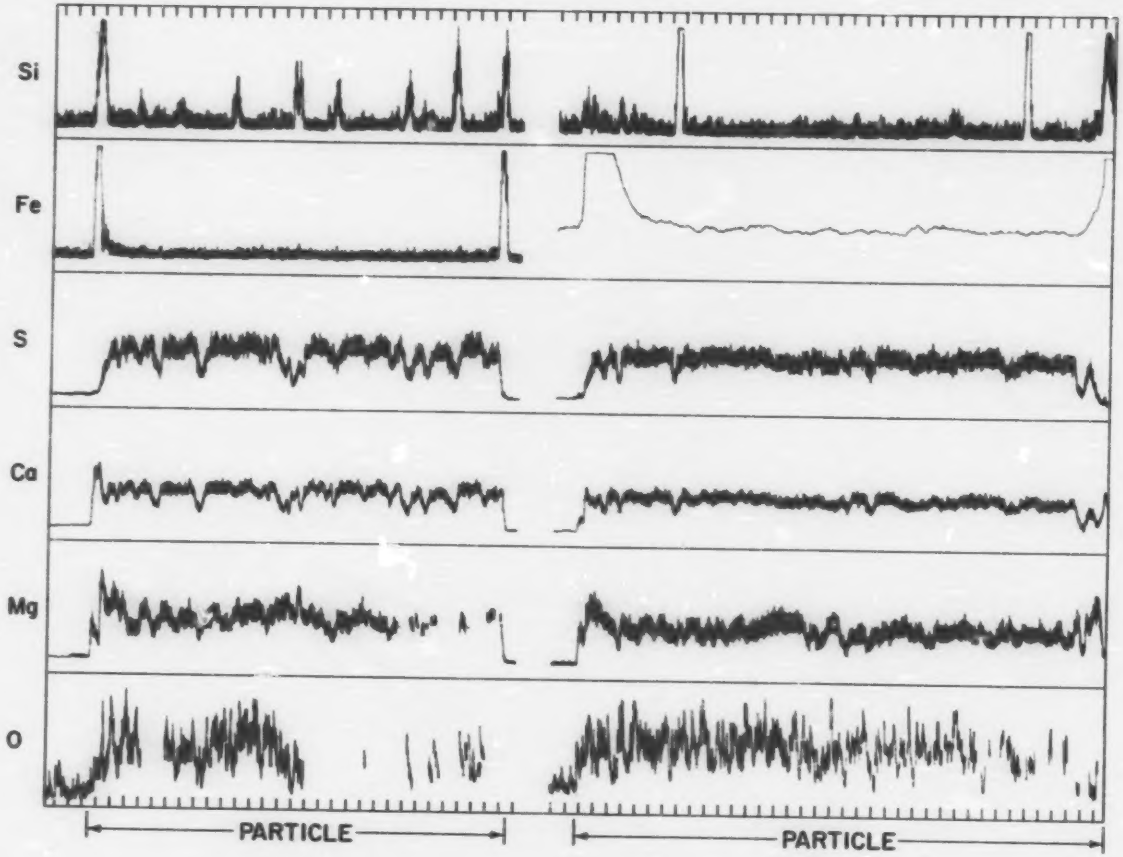


Fig. 23. Electron Microprobe Scan of Particles Taken from the Second-Cycle Sulfation Step of the Sulfation-Regeneration Experiment

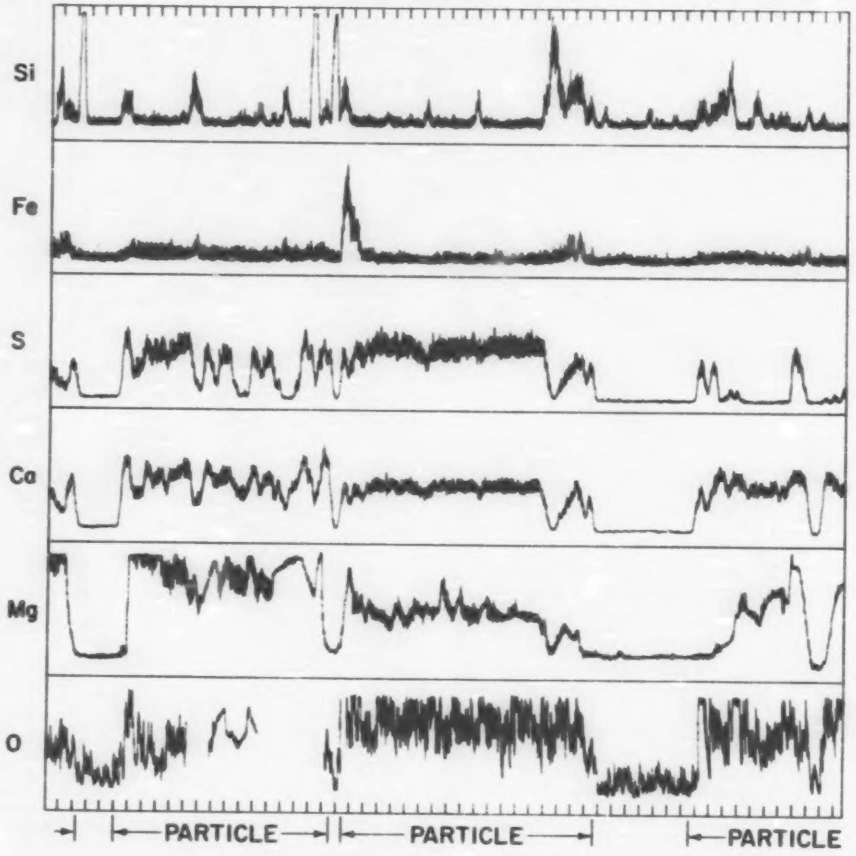


Fig. 24. Electron Microprobe Scan of Particles Taken from the Second-Cycle Reduction Step of the Sulfation-Regeneration Experiment

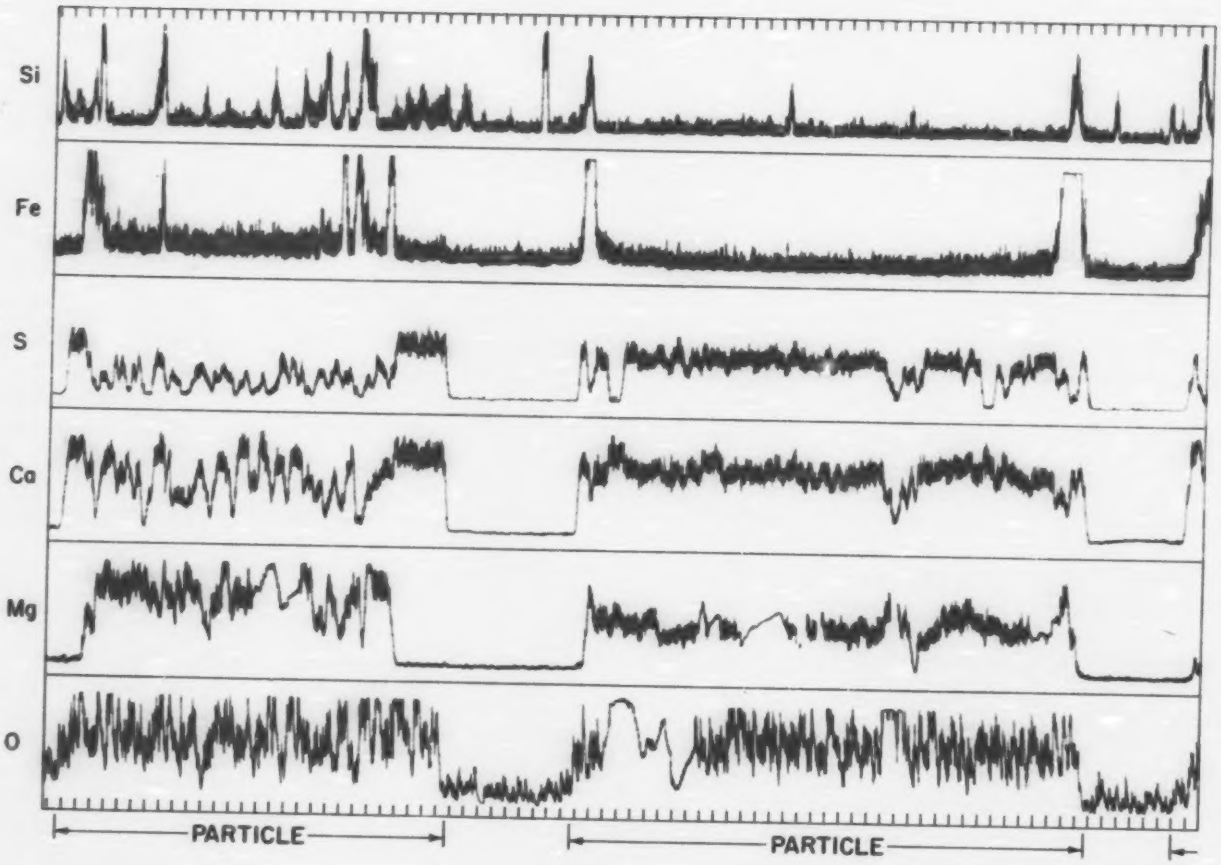


Fig. 25. Electron Microprobe Scan of Particles Taken from the Second-Cycle Regeneration Step of the Sulfation-Regeneration Experiment

Table 23. Summary of X-ray Analyses of Particles from Fluidized-Bed Experiments

Source of Solids	Chemical Compounds Found
Sulfation-regeneration experiment cycle 2 (sulfation)[a]	Major: $CaSO_4$ (Anhydrite), MgO (Periclase), Minor: CaS (Oldhamite)
Sulfation-regeneration experiment cycle 2 (reduction)[a]	Major: CaS (Oldhamite), $CaSO_4$ (Anhydrite), MgO (Periclase) Possible Very Minor: SiO_2 (Alpha-Quartz)
Sulfation-regeneration experiment cycle 2 (regeneration)[a]	Major: CaS (Oldhamite), MgO (Periclase) Possible Very Minor: $CaCO_3$ (Calcite)
CATS 22 - Product of second reaction with H_2S	Major: CaS (Oldhamite), MgO (Periclase) Minor: $CaCO_3$ (Calcite)
CATS 22 - Product after second regeneration	Major: $CaCO_3$ (Calcite), CaS (Oldhamite), MgO (Periclase)

[a] Details of this experiment have been reported earlier(1).

together throughout the particle at fairly uniform levels, whereas magnesium appears to be segregated from the calcium and sulfur. This indicates that sulfation takes place throughout the particle and is not limited to a surface reaction. The presence of iron on the particle surface, which had been inferred from microscopic examination of the particles, is confirmed by the electron probe scan (Fig. 23), which also shows some silicon and calcium concentrated at the surface. The mineral form of this surface layer is not identified, although a number of iron-calcium-silicon-oxygen (and/or sulfur) compounds exist. Microscopic examination of this surface layer on a hot stage indicates that its melting point is slightly less than 1100°C (2000°F).

The infrared spectrum of material taken from the second reduction step in the sulfation-regeneration experiment is shown in Fig. 21b. The intensity of the $SO_4^=$ bands is much reduced in comparison with Fig. 21a (sulfation step), as would be expected if the calcium sulfate was indeed reduced to calcium sulfide, but the reaction is clearly not complete. The X-ray data (Table 23) indicate that the concentration of CaS increased, but that $CaSO_4$ was still present in appreciable amounts. From the electron microprobe scan in Fig. 24, it is not clear whether or not the conversion from sulfate to sulfide was limited to a surface layer; the general features of the scan appear to be the same as those in Fig. 23.

Examination of the data for material taken from CATS-22 (Figs. 22a and 22b) shows that conversion of calcium carbonate to calcium sulfide by reaction with hydrogen sulfide did proceed (although not all carbonate was converted in this sample, see Fig. 22a). However, the regeneration reaction caused only partial conversion of sulfide to carbonate. Optical microscopy did not indicate that a surface layer formed on any of these samples, and no electron microprobe scans of the sample were made.

The most striking feature of Fig. 21 and of X-ray data for material taken from the second regeneration step in the sulfation-regeneration experiment is the complete absence of sulfate. The carbonate feature in the infrared spectrum of this material (Fig. 21) is more prominent than in the previously discussed samples, and calcium carbonate can be detected in the X-ray pattern (see Table 23). Again, the electron microprobe scan (Fig. 24) shows that calcium and sulfur appear together uniformly across the particle and that the iron-rich layer is still evident. The fact that all sulfate has disappeared at this stage of the process seems to indicate that the layer is not a barrier to reaction in the bulk of a particle.

All of the results appear to be consistent, but they do not appear to explain directly the difficulties encountered in the regeneration process. It seems likely that an iron-containing layer forms on the particles during the sulfation process (i.e., that sulfate or SO_2 is involved in the layer-forming reaction), but that the layer is not directly responsible for the problems encountered in subsequent steps. The presence of sulfate after the reduction step and the inability to effectively regenerate carbonate from CaS in both the cyclic and the CATS experiments suggest that the thermodynamics of the desired reactions may not be as favorable as previously believed.

2. One-Step Reductive Decomposition Process, Low Temperature Studies

In the continuous, one-step, reductive decomposition experiments made in the 3-in.-dia regenerator, the bed temperature is typically maintained at above 1900°F. At above 1900°F, the calculated SO_2 equilibrium pressure (presented earlier for the $CaSO_4$-CaS-CaO-CO-CO_2 and $CaSO_4$-CaS-$CaCO_3$-CO-CO_2 systems)[1] in the gas is sufficiently high so that the gas can be processed in a Claus plant to recover the sulfur content of the gas. Lower temperatures, although desirable from an equipment corrosion standpoint, would not produce a gas with a high enough SO_2 concentration for Claus plant processing.

In experiment REDUC-8 made in the 3-in.-dia unit a high sulfur removal from $CaSO_4$ was demonstrated at a bed temperature of only 1600°F. In the 3-in. unit, oxygen is present in addition to $CaSO_4$-CaS-CaO-CO-CO_2 to combust kerosene which provides heat to maintain the bed temperature. The oxygen can react with CaS and the system would then consist of $CaSO_4$-CaO-CO_2-CO for which the SO_2 equilibrium pressure is relatively high, as shown in Fig. 26, at a temperature of 1600°F. Therefore, a laboratory-scale scouting program (Experiments CATS-34 through -45) was initiated using the 1- and 2-in.-dia, batch, fluidized-bed regenerators to determine conditions which have an effect on the removal of sulfur and to identify the sulfur species in the off-gas. A bed consisting of $CaSO_4$ (Drierite) was reacted at a bed temperature range of 1200-1650°F with a gas composed of mixtures of two or more of the following gases: CO, CO_2, H_2O, and N_2. The inlet gas compositions, operating conditions, and SO_2 and O_2 concentrations in the off-gas are presented in Appendix C, Figs. C-1 to C-12 and Tables C-1 to C-5. Conclusive results were not obtained in these experiments but some observations were that:

1. Regeneration appeared to be most effective when the bed temperature and CO_2 concentration were such that the calcium product was $CaCO_3$ rather than CaO.

2. Generally, high SO_2 concentrations were observed when the O_2 concentration was high.

3. The maximum concentrations of SO_2 and maximum sulfur removals were obtained with an inlet gas mixture consisting of 27% CO, 19% CO_2, 6% O_2, and the remainder nitrogen. The maximum SO_2 concentration was approximately equal to the equilibrium concentration expected for the reaction:

$$CaSO_4 + CO \rightarrow CaCO_3 + SO_2$$

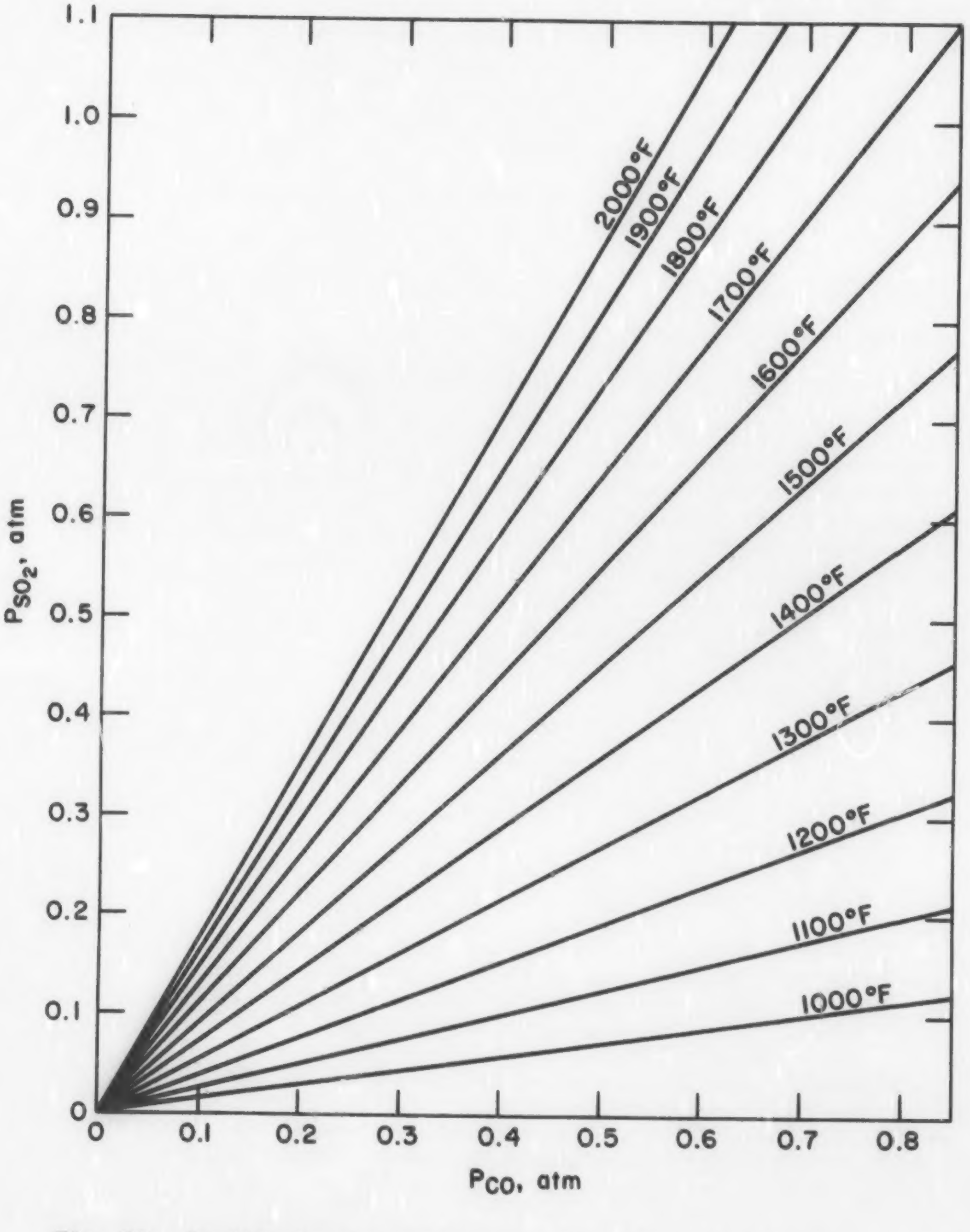


Fig. 26. Equilibrium Concentrations of SO_2 for the Reaction $CaSO_4 + CO \rightarrow CaCO_3 + SO_2$

4. Elemental sulfur was present in the off-gas, but the quantities detected were small.
5. Carbonyl sulfide was present in the off-gas. The concentration was small, except when high concentrations of CO (>30%) were used. The presence of carbonyl sulfide appeared to be dependent on the presence of sulfur dioxide.
6. The sulfur material balances for the experiments were generally >97%.

3. Reaction of $CaSO_4$ and CO_2/H_2 at Temperatures of 1400°F and Less

If the following one-step reaction

$$CaSO_4 + 4\ H_2 + CO_2 \rightarrow CaCO_3 + 3\ H_2O + H_2S$$

proceeds at low temperatures (<1400°F), the concentration of H_2S in the off-gas would be reasonably high. Equilibrium constants at 1000, 1200, and 1400°F are 4.37×10^8, 3.15×10^7, and 1.51×10^7, respectively. However, conversion of $CaSO_4$ to CaS must be avoided because the equilibrium concentration of H_2S for the reaction of CaS with CO_2/H_2O ($CaS + CO_2 + H_2O \rightarrow CaCO_3 + H_2S$) is low, less than 1500 ppm.

A bed of $CaSO_4$ (Drierite) was reacted with 85% H_2-CO_2 at 10 atm and 1000, 1200, and 1400°F for 75, 135, and 120 min, respectively. Experimental data are shown in Table 24. The results indicate that:

1. The peak concentration of H_2S in the off-gas increases with temperature.
2. The sulfide content of the bed increases with temperature, thereby indicating that reduction of $CaSO_4$ to CaS is taking place, rather than conversion to $CaCO_3$.
3. At 1400°F, the peak concentration of H_2S (1160 ppm, dry basis) was nearly equal to the equilibrium concentration of H_2S (1460 ppm, dry basis) expected for the reaction between CaS and CO_2/H_2O.

A further analysis of the competing reactions has been made and the information is presented in Appendix D. The conclusions were that the addition of water to the reactant mixture would have suppressed the CaS producing reaction, but that the H_2S concentration would still be too low for further processing of the gas in a Claus plant.

Table 24. Reaction Conditions and Analytical Results for Studies on $CaSO_4$-H_2-CO_2 Reaction

Pressure: 10 atm

Initial Bed: 700 g $CaSO_4$ (Drierite, 22.6 wt % S)

Inlet-Gas Flow Rates: 0.85 cfm H_2 at 70°F, 1 atm
0.15 cfm CO_2 at 70°F, 1 atm

Experiment No.	Bed Temp (°F)	Reaction Time (min)	Weight of Sulfur Removed as H_2S (g)	Avg. Conc. of H_2S in Off-Gas (ppm)	Weight of Final Bed (g)	Total Sulfur in Final Bed (wt %)	Sulfide in Final Bed (wt %)	Calculated Composition of Final Bed		
								$CaSO_4$ (wt %)	CaS (wt %)	$CaCO_3$ (wt %)
CATS-33	1400	0-25	0.71	650						
		25-50	1.14	1030						
		50-75	1.29	1160						
		75-120	1.82	910	544	27.6	12	66	27	7
		Total	4.96					(8.2 g S released)		
CATS-32	1200	0-30	0.21	160						
		30-60	0.59	440						
		60-90	0.67	500						
		90-135	1.04	520	666	22.6	1.2	96	3	1
		Total	2.51					(7.7 g S released)		
CATS-30	1000	75	low	low	677	22.2	Not Determined			

4. Removal of H_2S from Off-Gas by Reaction with Potassium Permanganate

When CaS is converted to $CaCO_3$ by the reaction of CaS with the CO_2-H_2O mixture, large quantities of H_2S will be formed. To avoid releasing H_2S into the laboratory exhaust system, a proposed scheme to remove the H_2S from the effluent gas stream is to pass the off-gas from the regenerator through a scrubber system containing potassium permanganate solution. The expected reaction is as follows:

$$8\ KMnO_4 + 3\ H_2S \rightarrow 8\ MnO_2 + 3\ K_2SO_4 + 2\ KOH + 2\ H_2O$$

To determine if the above reaction occurs, as well as the contact time necessary for reaction, a laboratory-scale experiment was performed. The procedure consisted of passing a CO_2-H_2S gas mixture through a bubbler containing potassium permanganate solution and monitoring the effluent gas stream for H_2S with the quadrupole mass spectrometer.

The bubbler contained 200 ml of 0.4 M $KMnO_4$ (0.0825 mole $KMnO_4$). A 90% CO_2-10% H_2S gas mixture was passed through the solution at ambient temperature and a flow rate of 0.013 cfm. The gas composition was controlled by feeding with previously calibrated rotameters. The reaction was rapid, as evidenced by immediate formation of a brown precipitate (MnO_2) and the absence of H_2S in the effluent gas stream at the start of the experiment. After 20 min of reaction, the presence of H_2S in the effluent gas stream was indicated by the quadrupole mass spectrometer. The H_2S flow was discontinued at that time. The total quantity of H_2S used during the reaction was 0.033 mole. The ratio of moles of $KMnO_4$ to moles of H_2S was ∿8:3, as would be expected from the above reaction. The products of the reaction were a clear solution and a brown precipitate of fine particles. A permanganate-containing solution was used in the process gas scrubber as a result of these tests.

V. TRACE-ELEMENT DISTRIBUTION STUDIES

A. Introduction

The potential of a fluidized-bed combustion system for retaining, in a solid constituent, trace elements released by the combustion of coal will be investigated. Coal will be combusted at 10 atm in a partially sulfated dolomite bed and also in an inert bed, such as alumina. Data on the distribution of trace elements in experiments with the two bed materials will be compared with each other and also with data published on trace-element emissions from conventional boiler plants.

B. Applicability of Selected Methods for Analyzing Trace Elements of Interest

The elements of interest, in order of priority as pollution agents, are listed in Table 25. Also listed in Table 25 are procedures believed to be the most applicable for analyzing these elements at trace concentration levels.

Ideally, a method of analyzing trace elements in coal combustion products should (1) determine a large number of elements of interest simultaneoulsy, (2) require relatively little sample preparation, (3) be capable of automation, (4) produce an output compatible with computerized data processing, and (5) be rapid.

Of the methods listed in Table 25, emission spectroscopy is capable of measuring with suitable sensitivity all elements, except fluorine and phosphorus. However, if this method is to meet the criteria of rapid output and computerized data processing, a rather sophisticated (and expensive) instrument equipped with direct-reading detectors would be necessary. Calibration of the instrument using materials of composition very close to those being analyzed (a time-consuming effort) also would be necessary. The resulting system would be highly specific to coal, ash, fly ash, etc., would be very rapid, and would have an accuracy of perhaps 10-100%, varying for different elements. The resulting system would be analogous to those used in steel mills for monitoring the quality of routinely produced alloys.

X-ray spectrometry is another method capable of simultaneously measuring most of the elements specified. It is capable of measuring all elements of atomic number greater than about 15 (the atomic number of phosphorus), but is is more sensitive for elements with higher atomic numbers. Generally, X-ray spectrometry is not sufficiently sensitive to be applicable at trace levels, particularly if sample sizes are small. The X-ray spectrometer has the merit of internal standarization which neutralizes matrix effects and makes for relatively high accuracy. For a production system, the X-ray

TABLE 25. Applicability of Selected Analytical Methods[a] for Trace Elements in Coal Combustion

Priority	Element or Ion	XRS	ES	SIE	AA/FP	FLUOR	COL
1	Fluoride			X[b]			
1	Lead	X	X		X		
1	Mercury	X	X		X		
1	Beryllium		X		X	X	
2	Cadmium	X	X		X		
2	Arsenic	X	X		X		
2	Nickel	X	X		X		
3	Copper	X	X		X		
3	Zinc	X	X		X		
3	Barium	X	X		X		
3	Tin	X	X		X		
3	Phosphorus						X
3	Lithium		X		X		
3	Vanadium	X	X		X		
3	Manganese	X	X		X		
3	Chromium	X	X		X		
3	Selenium	X	X		X		

[a] XRS - X-ray Spectrometry.
ES - Emission Spectroscopy.
SIE - Specific Ion Electrode Method.
AA/FP - Atomic Absorption Spectrometry/Flame Photometry.
FLUOR - Fluorimetry.
COL - Colorimetric Method.

[b] X - Probably applicable for analysis at trace concentration levels.

spectrometer should be coupled to a computer.

An improved nondispersive X-ray spectrometer (NDXR) is particularly suited for coupling to a computer because analysis of the fluorescent X-ray spectrum from the sample is done by a solid-state detector/pulse-height analyzer that provides digital data for computer processing. Analysis by X-ray spectrometry is discussed further in a following section of this report.

Atomic absorption spectrometry is a method with high sensitivity, particularly since new atomization procedures have been developed, for example, graphite furnaces and plasma units. The method is suited for accurate analysis of specific elements because (unlike emission and X-ray spectroscopy) it does not provide information for more than two elements simultaneously. Atomic absorption is particularly suited to the determination of mercury and would also be appropriate for lithium. It is most applicable to metals because the sensitivity of the method declines with increasing nonmetallic character of the element. The method is also less sensitive to elements that form refractory oxides (and hence atomize with greater difficulty). This method should probably be viewed as a supplement to emission or X-ray spectrometry.

The specific ion electrode method is preferred for measuring trace quantities of fluoride in aqueous solution. Generally, it is used with a pyrohydrolysis technique for liberating the fluoride as HF and collecting it in aqueous solution.

Fluorimetry is a very powerful method of analyzing very small quantities of certain elements. For example, it is the method of choice for uranium and beryllium. It is claimed that concentrations of beryllium as low as 10^{-5}% can be determined in air dust without chemical separations.

A variety of ultrasensitive colorimetric methods are available for many elements that are suited for trace-element analysis of coal and coal combustion residues. We have chosen to list only phosphorus under the "Colorimetric" heading because other methods are more appropriate for the other elements. The colorimetric method is capable of measuring phosphorus in microgram quantities.

1. Analysis of Coal, Limestone, and Coal Combustion Residues by X-ray Spectrometric Analysis

X-ray spectrometry is a particularly attractive method for analyzing coal and coal combustion residues (CCCR) because (1) in principle, little sample preparation is required, (2) a number of elements are determined simultaneously, (3)application is to all elements of atomic number greater than 15 (the atomic number of phosphorus), and (4) by the use of internal standards, quantitative information of relatively good accuracy can be acquired.

In X-ray spectrometry, as usually practiced, a sample of the material to be analyzed is irradiated with X-rays from a tungsten (or possibly molybdenum) target X-ray tube. Elements in the sample are excited and emit fluorescent X-rays whose energies are characteristic of the elements in the sample. The X-ray spectrum so produced is analyzed by a properly oriented crystal that disperses a beam of X-rays according to Bragg's law of diffraction. The intensities of the dispersed X-rays are measured by a radiation detector that physically traverses the area upon which they impinge. By suitable calibration, the intensities are converted to concentrations.

The X-ray spectrometer being developed at ANL differs from the conventional instrument in two respects: (1) the exciting radiation is itself a characteristic X-ray formed when a secondary target is irradiated with X-rays from a conventional X-ray tube, and (2) the detector is a solid-state radiation detector/pulse-height analyzer that electronically sorts the fluorescent X-rays from the sample according to energy and measures the intensities. The advantages of the new system are simultaneous measurement of all X-rays and markedly increased sensitivity. As little as tenths of a microgram of some elements can be detected. By adding known quantities of elements having about the same X-ray fluorescence energy as the element to be detected, the quantities of the elements present can be accurately estimated by direct comparison of the relative intensities.

2. Application of Nondispersive X-ray (NDXR) Spectrometry to Coal and Coal Combustion Residues

The capability of NDXR spectrometry for quantitative simultaneous measurement of components at trace levels has been demonstrated in a number of applications. Recently, the concentrations of U, Au, Zn, and Fe in a sample were estimated to be 10, 0.1, 8-10, and 5 μg/ml of solution, respectively; the sample analyzed consisted of less than 1 ml of solution with an internal standard. Detection of Cl, K, Ca, Fe, Cu, Zn, Pb, and Br in bile has also been demonstrated.

Because this instrument may be applicable to the analysis of CCCR, preliminary analyses were performed on several samples retained from earlier coal combustion experiments. Approximately 0.010 g of sample was used in each analysis and the data obtained were intended to be only qualitative.

The results are reported in Table 26. These are preliminary data obtained with a far-from-optimized system. Constituents identified as major are believed to be present at concentrations greater than 1% and minor constituents, at less than 1%. The column headings "Principal," "Trace," and "Questionable" represent three levels of concentration derived by visual comparison of peak heights on an oscillogram. No internal standards were used to quantify the amounts present.

If analysis for a particular element (or elements) were of interest, the sensitivity could be optimized by using a secondary target that would produce X-rays of an energy corresponding to the X-ray absorption edge of the element of interest. (This would enhance absorption and increase fluorescence X-ray intensity and, hence, sensitivity.)

C. Flue-Gas Sampling

To determine the behavior of trace elements in coal during fluidized-bed combustion, it will be necessary to analyze the final

Table 26. Analysis of Coal and Coal Combustion Products with Nondispersive X-ray Spectrometer

Material	Major Constituents[a]	Minor Constituents[b]		
		Principal	Trace	Questionable
Commonwealth Edison Coal, Shipment #4	Fe	Sr, Se	Cu, Ti, Mn Zn, Ca, Ba Pb, Mo	Br, Rb
Primary Cyclone Product from Experiment AR-6	Fe, Ca	Sr	Zn, Ti, Mo Cu	Rb
Secondary Cyclone Product from Experiment AR-6	Fe, Ca	Sr	Zn, Ti, Cu Mo, Pb	Rb, Se
Final Bed from Experiment AR-6	Ca, Fe	Si	Se, Zn, Mo	--
Final Filter from Experiment AMER-33	Fe, Ca	Sr, Br	Ti, Cu, Zn, Mo, Se	--
Limestone No. 1359	Ca	Fe	Sr, K, Ba	Rb

[a] Believed to be present at >1 wt % conc.

[b] Believed to be present at <1 wt % conc.

flue gas for particulate and gaseous trace-element compositions, as well as the various solids streams associated with the process. Flue-gas sampling procedures have been determined and the assembly of the necessary sampling equipment has been completed.

1. Description of Sampling Location

A very important consideration in trace-element sampling is the location of the sampling point. Since the Brink Impactor to be used in the particulate sampling is designed to handle particles in the range from 0.3 to 3 μm in diameter, the sampling will be done after the flue gas has passed through gas-solid separators which remove particles larger than about 3 μm in diameter and through the pressure letdown valve. This has the advantage of allowing the sampling to be accomplished at near-atmospheric pressure, even though the combustor and the ancillary equipment are operating at pressures of up to 10 atm. The material removed in the separators can also be recovered and analyzed, if so desired.

The modifications made in the flue-gas line to accommodate the sampling process are indicated in Fig. 27. During sampling

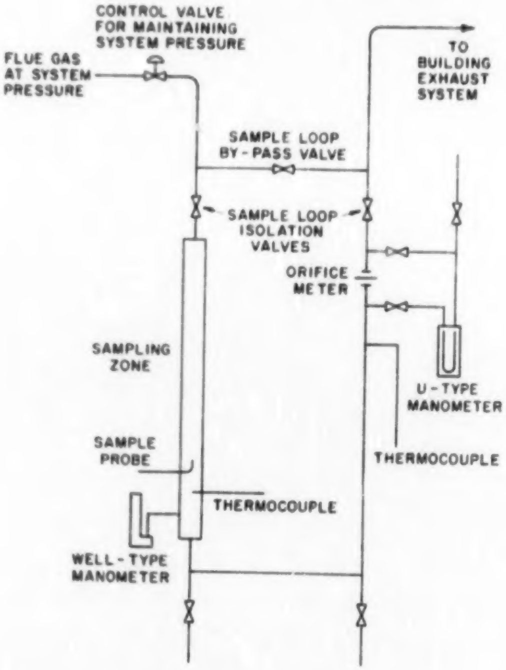

CONTROL VALVE FOR MAINTAINING SYSTEM PRESSURE
FLUE GAS AT SYSTEM PRESSURE
TO BUILDING EXHAUST SYSTEM
SAMPLE LOOP BY-PASS VALVE
SAMPLE LOOP ISOLATION VALVES
ORIFICE METER
SAMPLING ZONE
U-TYPE MANOMETER
SAMPLE PROBE
THERMOCOUPLE
THERMOCOUPLE
WELL-TYPE MANOMETER

Fig. 27. Experimental Flow System for Flue-Gas Sampling

periods, the sample-loop isolation valves are opened and the bypass valve is closed to direct the flue gas through the sampling zone. The sampling zone is a 5-ft length of 4-in.-dia Type L copper tube with a nominal inside diameter of 3.905 in. The increased cross section of the sampling zone is intended to reduce the average gas velocity past the sample probe to between 6 and 12 ft/sec, depending on the operating conditions in the combustor.

To allow for isokinetic sampling of the flue gas, the total gas flow through the sample loop will be determined using the orifice meter. Based on the relative conditions at the meter and the sampling location, the linear gas-flow rate past the sample probe can be determined by assuming fully developed flow at the sampling point. This is a very reasonable assumption, because the sample probe is located approximately 12 pipe-diameters downstream and 3 pipe-diameters upstream from any flow disturbances.

2. Particulate Sampling

The apparatus for the sampling of flue-gas particles is illustrated in Fig. 28. The sample probe is constructed from 1/4-in. Type 304 stainless steel tubing. A tapered nozzle with a 5/32-in. opening is affixed to the end of the probe to provide for streamlined sampling. The probe can be inserted to any depth along the diameter of the flue to allow for sampling at several traverse points. The probe, which normally faces upstream, can also be pointed downstream when samples are not being taken to prevent possible accidental plugging of the nozzle opening.

The particles in the gas sample are collected in the Brink Cascade Impactor and the follow-up,glass-fiber filter (Gelman Type A). The impactor has five in-line stages, each of which has a jet that utilizes a collection cup as an impaction plate. A spring holds each collection cup in place. A single stage of the impactor is illustrated in Fig. 29.

The particles suspended in the gases pass through a jet. Particles with sufficient inertia impact against a cup, and the remainder pass through annular slots located around the cup. Figure 30 illustrates the cup design.

Each collection cup has annular slots with a total cross-sectional area 30 times the area of the largest jet, thereby reducing turbulent effects to a negligible level. The dimensions of the impactor jets are given in Table 27. The impactor, which is machined from Type 316 stainless steel, collects particles in the range from 0.3 to 3.0 μm.

The glass-fiber filter at the outlet of the impactor collects the particles that pass the final stage; in general, these are particles

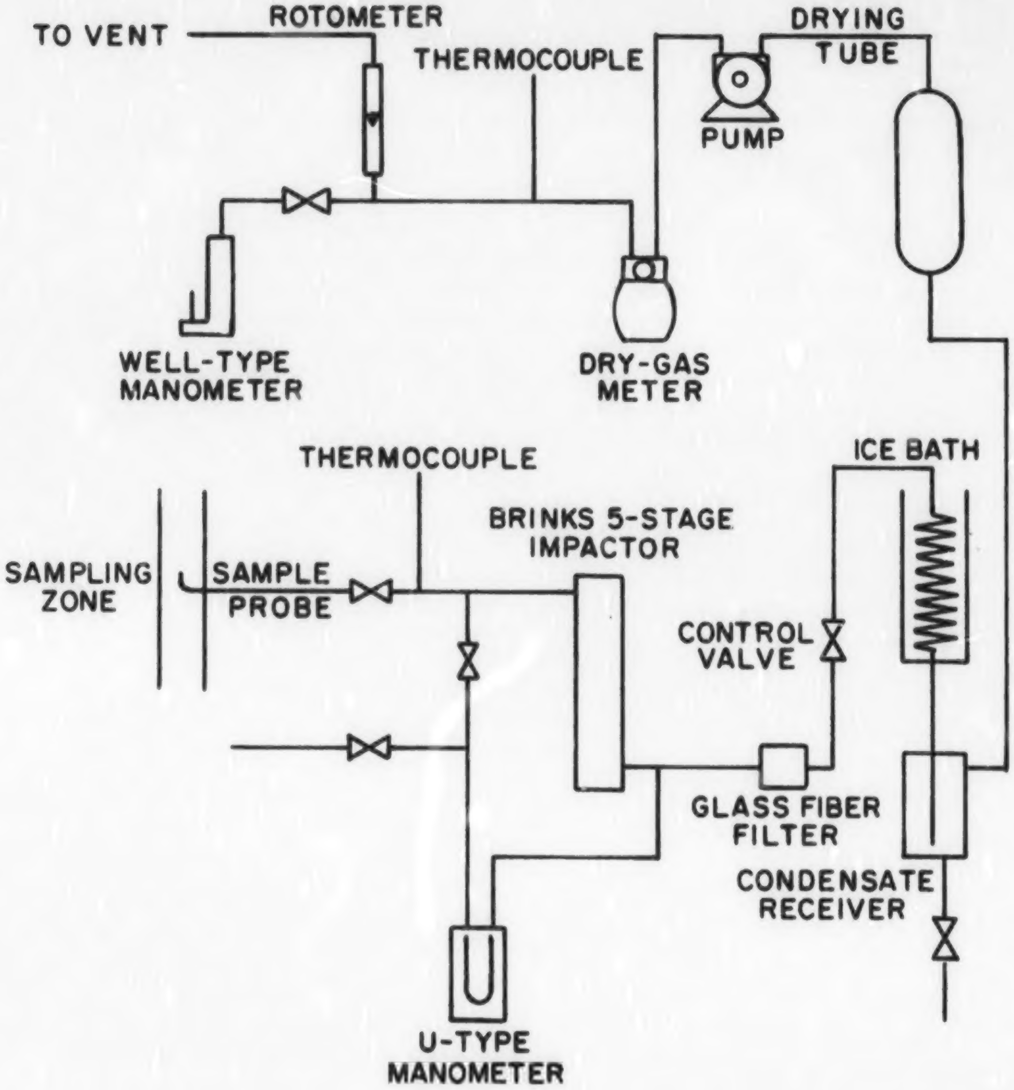

TO VENT
ROTOMETER
THERMOCOUPLE
DRYING TUBE
PUMP
WELL-TYPE MANOMETER
DRY-GAS METER
THERMOCOUPLE
ICE BATH
BRINKS 5-STAGE IMPACTOR
SAMPLING ZONE
SAMPLE PROBE
CONTROL VALVE
GLASS FIBER FILTER
CONDENSATE RECEIVER
U-TYPE MANOMETER

Fig. 28. Apparatus for Particulate Sampling of Flue Gas

smaller than 3 μm.

The control valve is used to regulate the volumetric flow through the impactor from 0.9 to 1.2 cfm, so that the velocity at the nozzle inlet of the sample probe equals the linear velocity of the flue gas flowing past the probe. This is done to promote representative

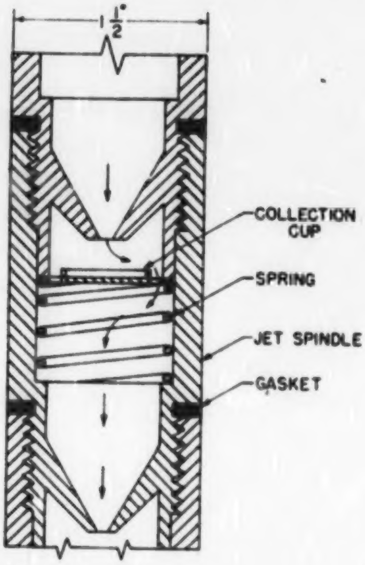

$1\frac{1}{2}$"
COLLECTION CUP
SPRING
JET SPINDLE
GASKET

Fig. 29. Single Impactor Stage

sampling of the particles in the flue gas by isokinetic sampling. It may be necessary to heat the probe, impactor, and filter to prevent condensation of flue-gas water.

The remainder of the sample train is designed to accurately determine the sampling rate and the total volume of the gas sample taken, so that the particulate loading of the main flue-gas stream can be calculated.

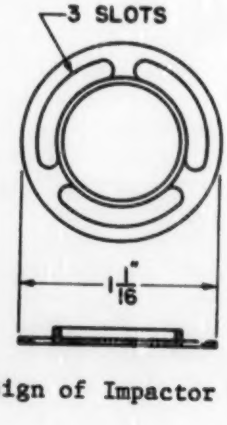

3 SLOTS
$1\frac{1}{16}$"

Fig. 30. Design of Impactor Collection Cups

TABLE 27. Dimensions of Cascade Impactor Jets

	Dimensions, (cm)	
Jet No.	Jet Dia	Spacing of Jet Opening[a]
1	0.2490	0.747
2	0.1775	0.533
3	0.1396	0.419
4	0.0946	0.282
5	0.0731	0.220

[a] From collection-cup surface.

3. Treatment of Particulate Samples

It is anticipated that, in addition to obtaining total particulate and trace-element concentrations in the flue gas, it will also be possible to obtain trace-element data as a function of particle size. It will be necessary, therefore, to obtain complete analytical and particle-size-distribution data for the material impacted on each cup or stage of the impactor. Since it is not uncommon to collect from 40 to 80 percent of the particulate matter on one stage of the impactor, the sample time will be limited by re-entrainment from this cup. The maximum sample time must be used, therefore, to insure the collection of reasonable quantities of material on the other cups.

To obtain particle-size-distribution data, samples of the material from each stage and the final filter will be examined using a scanning electron microscope (SEM). Experience with the instrument available indicates that reasonably good photomicrographs can be obtained at magnifications as high as 20,000X. It should be possible, therefore, to obtain from such photographs reasonably accurate particle-size information.

Consideration is also being given to the possible application of a scanning computer system developed by C. B. Shelman and Donald Hodges of the Applied Mathematics Division of Argonne National Laboratory to the counting and size analysis of the particles. The system, called ALICE, is capable of searching photographs for predetermined details and then analyzing these details and recording the resulting data. In the examination of nerve fibers, for example, ALICE counted each fiber in the nerve samples, calculated the area of each fiber, and remembered its location, so that it could provide information on the distribution of fibers of any particular size. A great deal of attention will be given to preparing the photomicrographs in a way that will ensure their adequacy for computer analysis.

To obtain the necessary elemental information, the material from each stage of the impactor will also be subjected to chemical analysis. The particular elements of interest and the analytical methods being considered for their determination have been described above.

4. Determination of Mercury in Particulate and Gaseous Emissions

Supplemental to the primary determination of particulate emissions in the flue gas is the determination of possible trace-element gaseous emissions. Of particular concern in this area is mercury. Billings *et al.*[4] have reported that up to 90% of the mercury in the coal is released during combustion and appears as vapor discharged in the stack gas, while only 10% remains in the residual ash. It would seem essential, therefore, that in the case of mercury, a method for sampling both particulate and gaseous emissions should be employed.

The method being considered is essentially the one proposed by the Environmental Protection Agency.[5] The apparatus to be used in the sampling train is illustrated in Fig. 31. In principle, the particulate and gaseous emissions are isokinetically sampled from the flue gas and collected in the acidic iodine monochloride solution. The mercury collected (in the mercuric state) is reduced to elemental mercury in basic solution by hydroxylamine sulfate. Mercury is subsequently vaporized from the solution by a mercury-free air stream and analyzed using an atomic absorption spectrophotometer in the flameless mode.

The entire sampling train up to the check valve will be constructed of Pyrex glass. The probe dimensions, which have not yet been determined, will be somewhat larger than the stainless steel probe to accommodate the larger volumetric sampling flow rates of 0.5 to 1.0 cfm.

The second impinger in the sampling train is of the Greenburg-Smith design with the standard tip. The remainder of the impingers are gas-washing bottles modified by replacing the standard tip with a 1/2-in.-ID glass tube, which extends to 1/2 in. from the bottom of the flask. Each flask has a capacity of 500 ml. The first, second, and third impingers contain the mercury scrubbing solution. The fourth impinger contains soda lime to neutralize acid vapors, while the fifth impinger contains silica gel to remove water vapor.

The filter holder will also be made of Pyrex and is designed to accept 50-mm glass-fiber filter paper. The filter provides for the removal of particulates and liquid mist entrained in the flowing gas from the first three impingers.

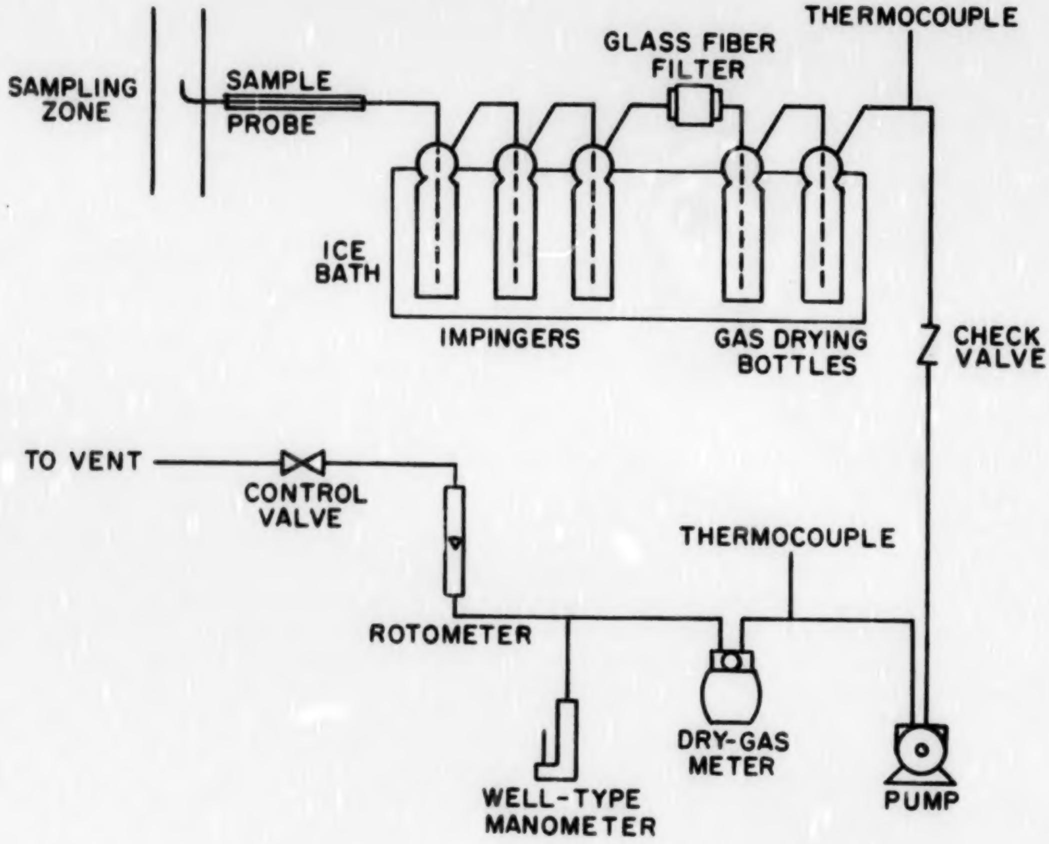

THERMOCOUPLE
GLASS FIBER FILTER
SAMPLING ZONE
SAMPLE PROBE
ICE BATH
IMPINGERS
GAS DRYING BOTTLES
CHECK VALVE
TO VENT
CONTROL VALVE
THERMOCOUPLE
ROTOMETER
DRY-GAS METER
PUMP
WELL-TYPE MANOMETER

Fig. 31. Apparatus for the Determination of Particulate and Gaseous Emissions of Mercury in Flue Gas

Assembly of the sampling equipment has been completed and the collecting of samples from the flue gas will be initiated in the near future.

5. Determination of Inorganic Fluorides in Gaseous and Particulate Emissions

It is also possible that some fluorine may be present in the gaseous phase of the flue gas from the combustor. It has been demonstrated by Pack *et al.* that gaseous and particulate inorganic fluorides can be sampled from the atmosphere using a water-filled impinger.[6] It will be possible, therefore, to use the same sampling train for both the mercury determination and the fluoride determination. Analytical methods for trace quantities of fluoride are currently being researched. When an appropriate analytical method is selected, sampling for fluoride will also be initiated.

VI. ACKNOWLEDGMENTS

We gratefully acknowledge the help given by Dr. R. C. Vogel, Mr. L. Burris, Mr. D. S. Webster, Dr. S. Lawroski, and Mr. L. Link in directing and reviewing the program, to Mr. D. E. Grosvenor, Mr. J. F. Lenc, and Mr. J. J. Stockbar for their many contributions and efforts during their temporary appointment to the group, and to our secretary, Mrs. Vita Shiffer.

We are indebted to Dr. P. Cunningham, Dr. V. Maroni, Dr. C. Johnson, Mr. S. Johnson, Mr. R. Schablaske, and Mr. W. Shinn for their analysis of bed particle samples, and to Dr. P. Cunningham for preparing the section of this report relative to the results of their analysis of the bed particles. Also, to Dr. P. Cunningham, Dr. M. Blander, and Dr. R. Yang for their study of the thermodynamic considerations relating to the conversion of $CaSO_4$ to $CaCO_3$.

VII. REFERENCES

1. A. A. Jonke *et al.*, Reduction of Atmospheric Pollution by the Application of Fluidized-Bed Combustion and Regeneration of Sulfur-Containing Additives, Annual Report, July 1971-June 1972, EPA-R2-73-253. (Available from National Technical Information Service as PB 227-058/AS)

2. T. W. Zadick, R. Zavalita, and F. P. McCandless, Department of Chemical Engineering, Montana State University, private communication.

3. A. A. Jonke *et al.*, Reduction of Atmospheric Pollution by the Application of Fluidized-Bed Combustion, Annual Report, July 1969-June 1970, ANL/ES-CEN-1002.

4. C. E. Billings, A. M. Sacco, W. R. Matson, R. M. Griffin, W. R. Coniglio, and R. A. Harley, Mercury Balance on a Large Pulverized Coal-Fired Furnace, Preprint of paper presented at the 65th Annual Meeting of the Air Pollution Control Association, Miami Beach, Florida, June 1972.

5. Environmental Protection Agency, National Emission Standards for Hazardous Air Pollutants, Federal Register 36: No. 234, pp. 23239-23256, Dec. 7, 1971.

6. M. R. Pack, A. C. Hill, M. D. Thomas, and L. G. Transtrum, Determination of Gaseous and Particulate Inorganic Fluorides in the Atmosphere, American Society for Testing Materials, Special Technical Publication No. 281, pp. 27-44, 1960.

APPENDIX A. ENGLISH TO METRIC UNIT EQUIVALENTS

Table A-1. English to Metric Unit Equivalents

	English System	Metric Equivalent
Length	in.	2.54 cm
	ft	0.305 m
Area	in.^{2}	6.45 cm^2
	ft^2	0.093 m^2
Volume	in.^{3}	16.39 cm^3
	ft^3	28.32 l (liter)
Mass	oz	28.35 g
	lb	453.6 g
Pressure	lb/in.^{2}	51.70 mm Hg
	in. H_2O	1.865 mm Hg
	atm	760 mm Hg
Temperature	°F	1.8 (°C) + 32
	°R	1.8 (°K)
Energy	BTU	252 cal
Power	BTU/min	252 cal/min

APPENDIX B. SPECIFIC ANALYTICAL PROCEDURES FOR SOLIDS SAMPLES FROM COMBUSTION AND REGENERATION EXPERIMENTS

Table B-1. Specific Analytical Procedures

A. Elemental and Functional Groups:

1) Calcium. Determined by means of an EDTA volumetric titration.

2) Sulfur. Leco combustion method employing an automatic volumetric titration of an $IO_3^=$-I-starch system.

3) Carbon. Leco combustion method using a thermal-conductivity detector employing the O_2/CO_2 relationship.

4) Carbonate. Determined by measuring with a sensitive gas chromatograph the CO_2 evolved by acidification of the material.

5) Sulfate, $SO_4^=$. A gravimetric method is employed. The sulfate present is converted to barium sulfate which is treated to 900°C to remove any organic material and weighed.

6) Combined Nitrogen. A micro-Kjeldahl method is used. The nitrogen is released as ammonia, absorbed, and titrated.

B. Coal and Coal Ash

These analyses are performed by a commercial laboratory (Commercial Testing and Engineering Co., South Holland, Ill.) employing ASTM designation D271-64 methods. The analyses made are proximate, ultimate, mineral (ash), fusibility of ash, free swelling index, and calorific value.

APPENDIX C. OPERATING DATA AND RESULTS OBTAINED IN BATCH REGENERATION EXPERIMENTS IN THE 1- AND 2-INCH-DIAMETER REACTOR

Regarding the Reaction

$CaSO_4 + CO \rightleftarrows CaCO_3 + SO_2$

(CATS-34 through -45)

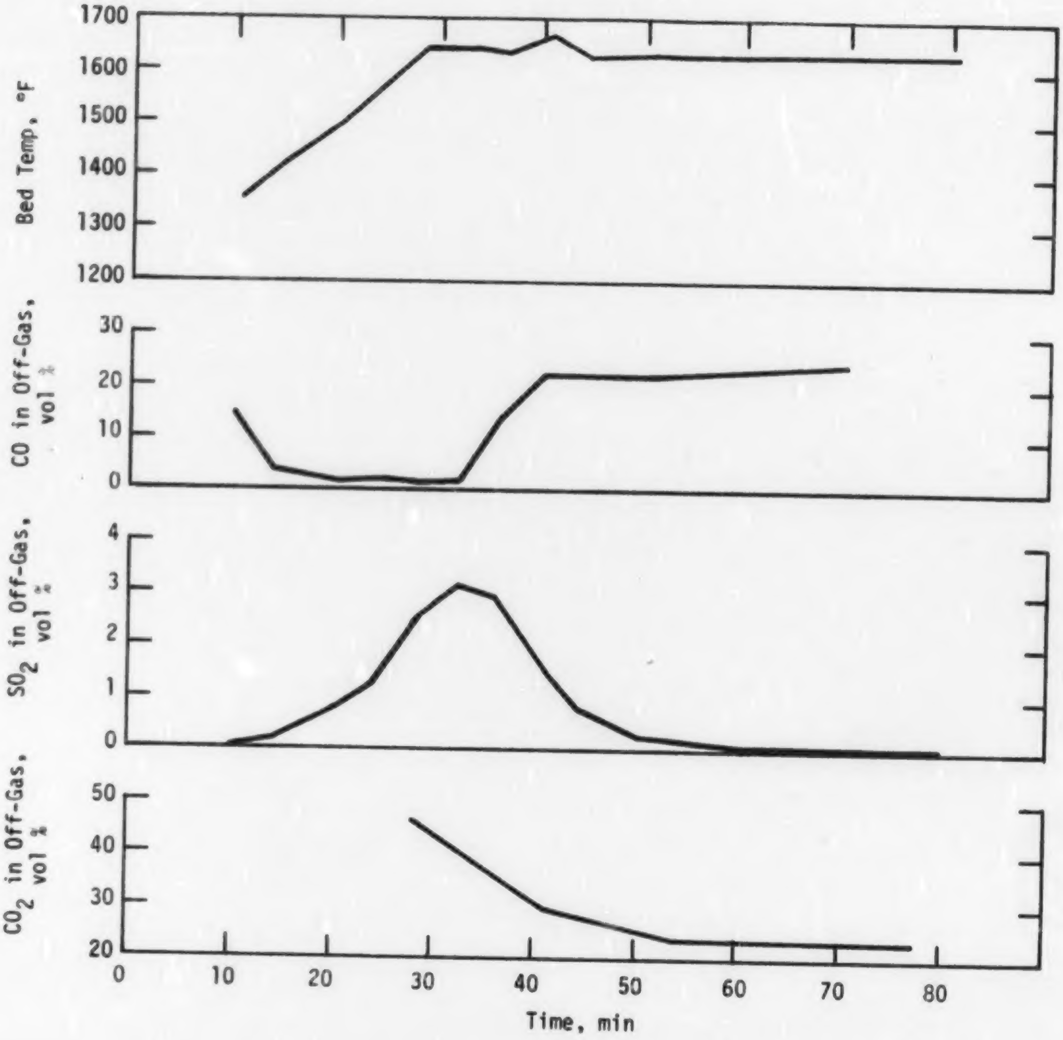
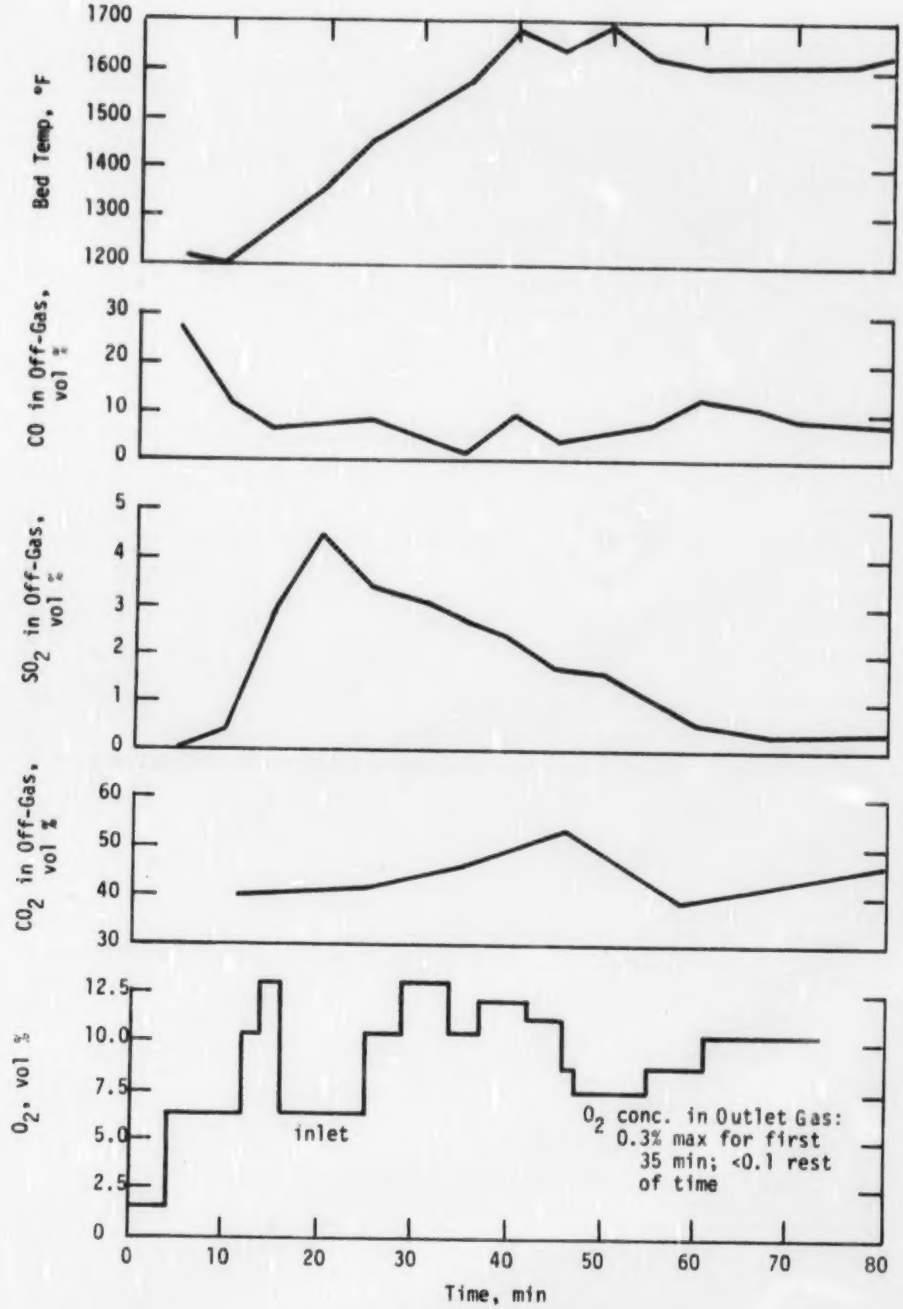


Fig. C-1. Operating Conditions for Experiment CATS-34



O_2 conc. in Outlet Gas: 0.3% max for first 35 min; <0.1 rest of time

Fig. C-2. Operating Conditions for Experiment CATS-35

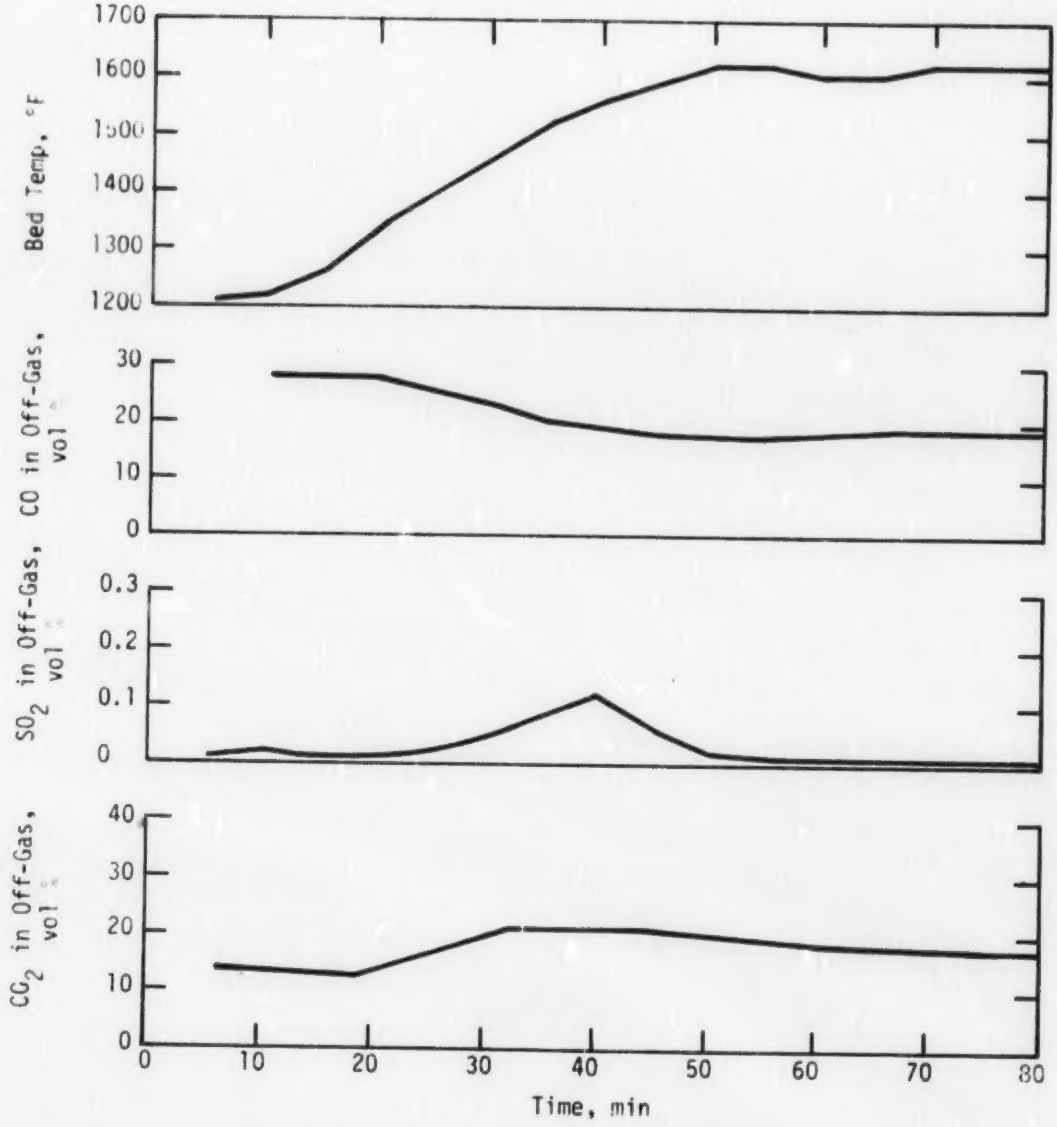


Fig. C-3. Operating Conditions for Experiment CATS-36

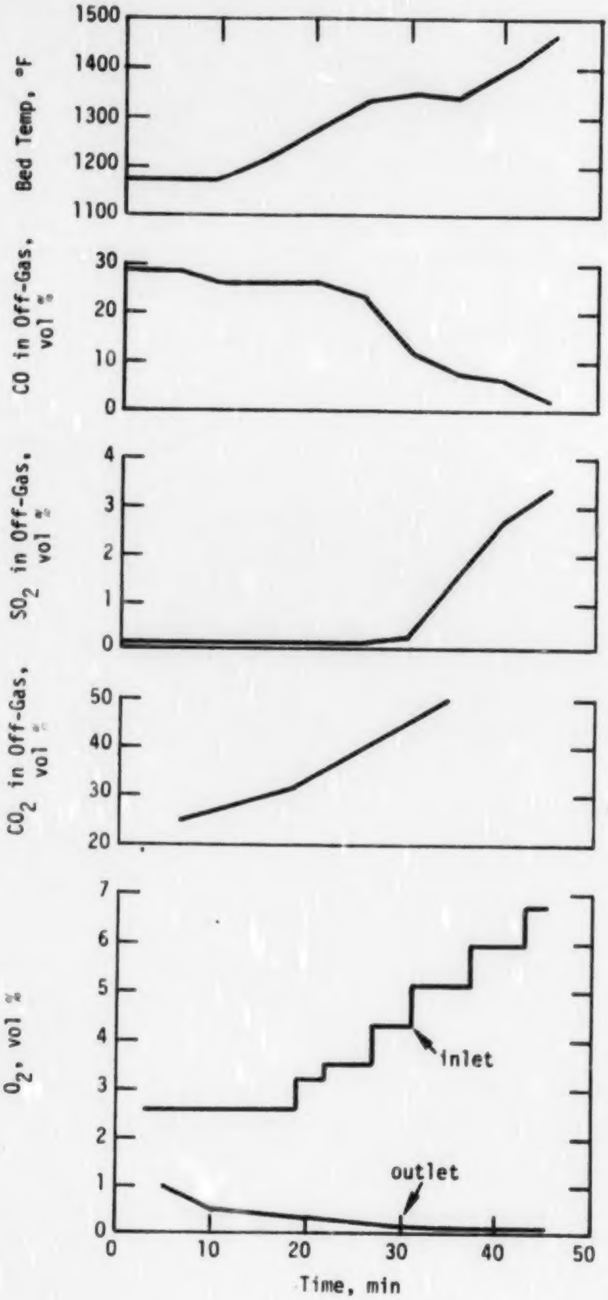


Fig. C-4. **Operating Conditions for Experiment CATS-37**

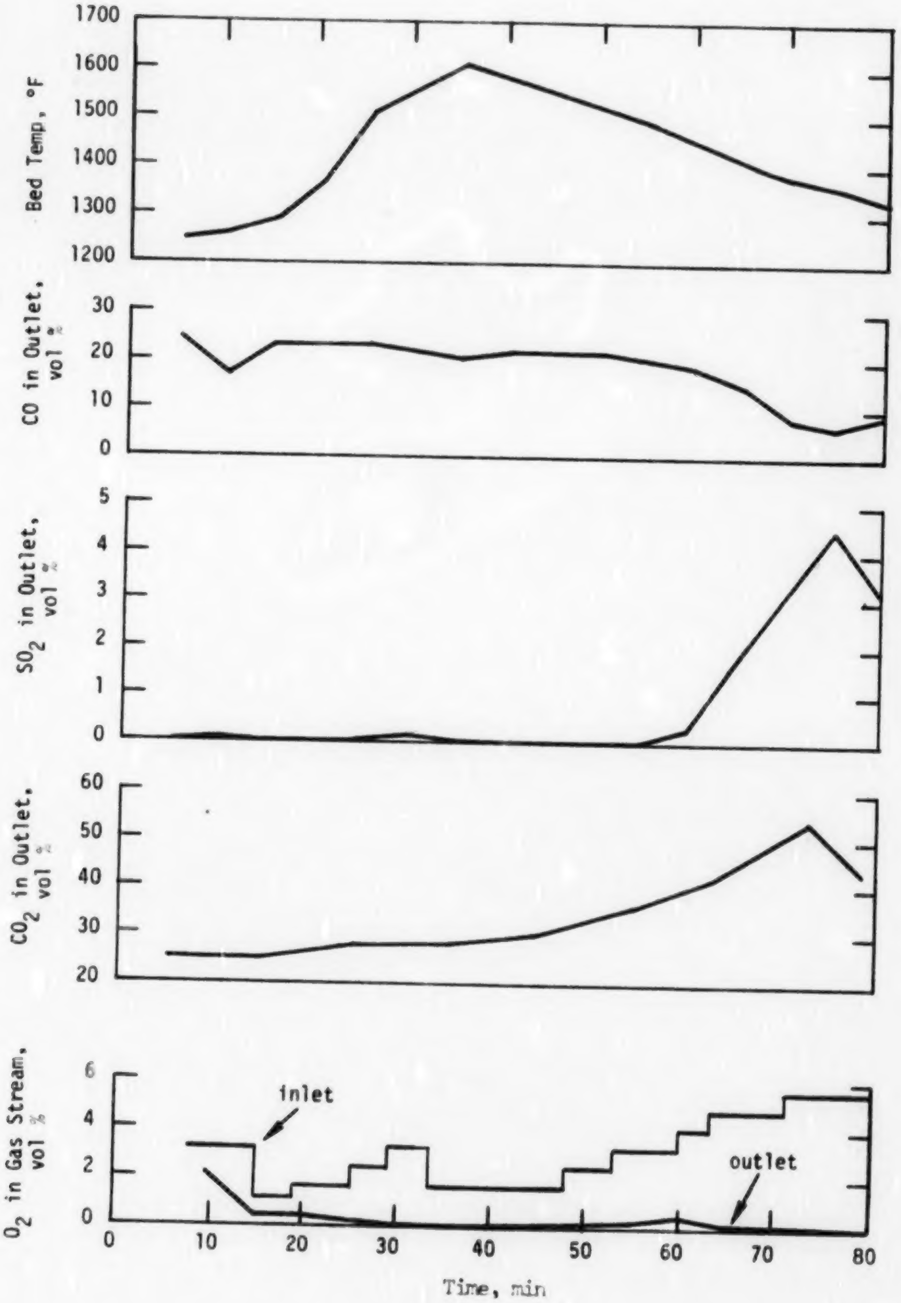


Fig. C-5. **Operating Conditions for Experiment CATS-38**

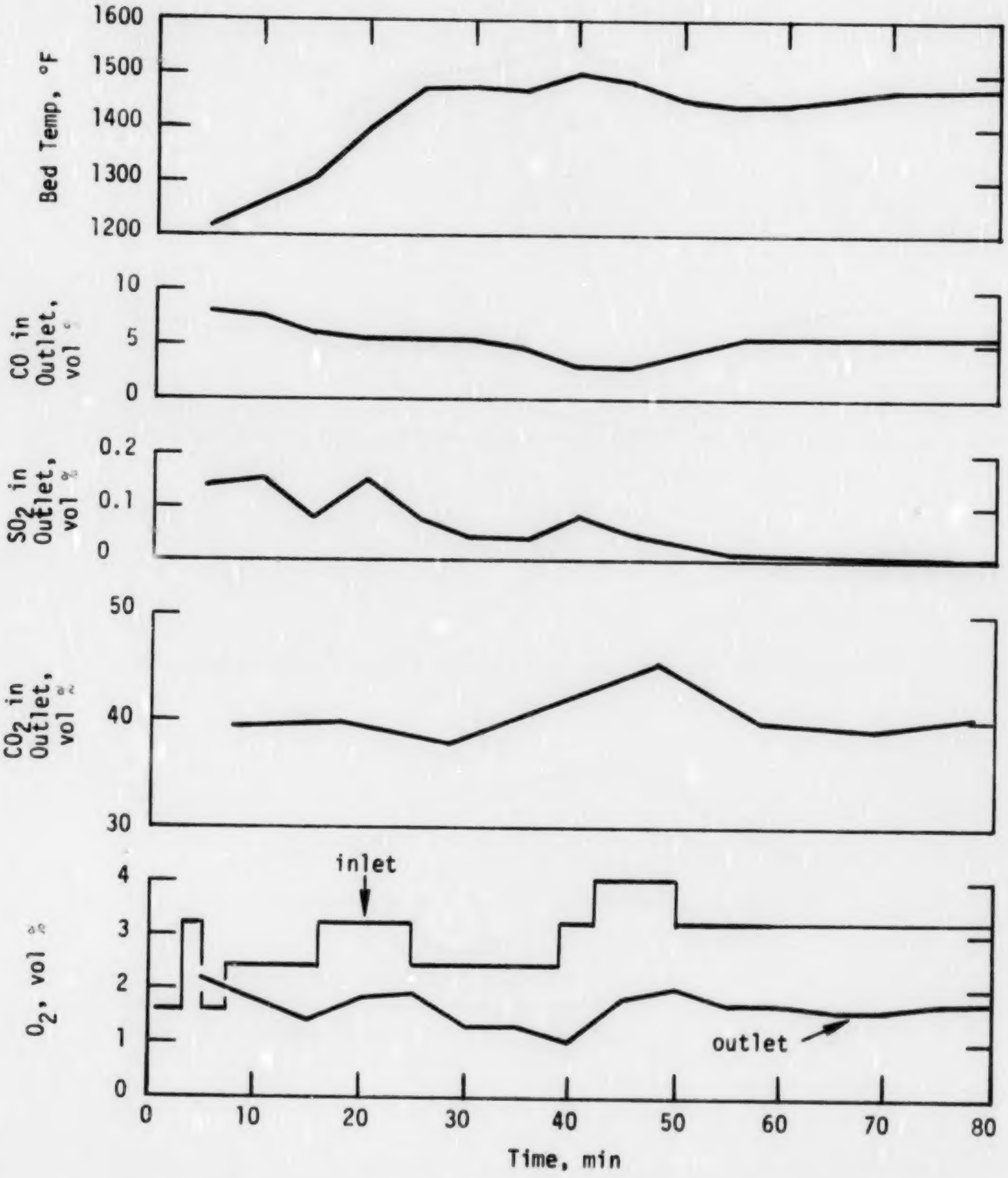


Fig. C-6. Operating Conditions for Experiment CATS-39

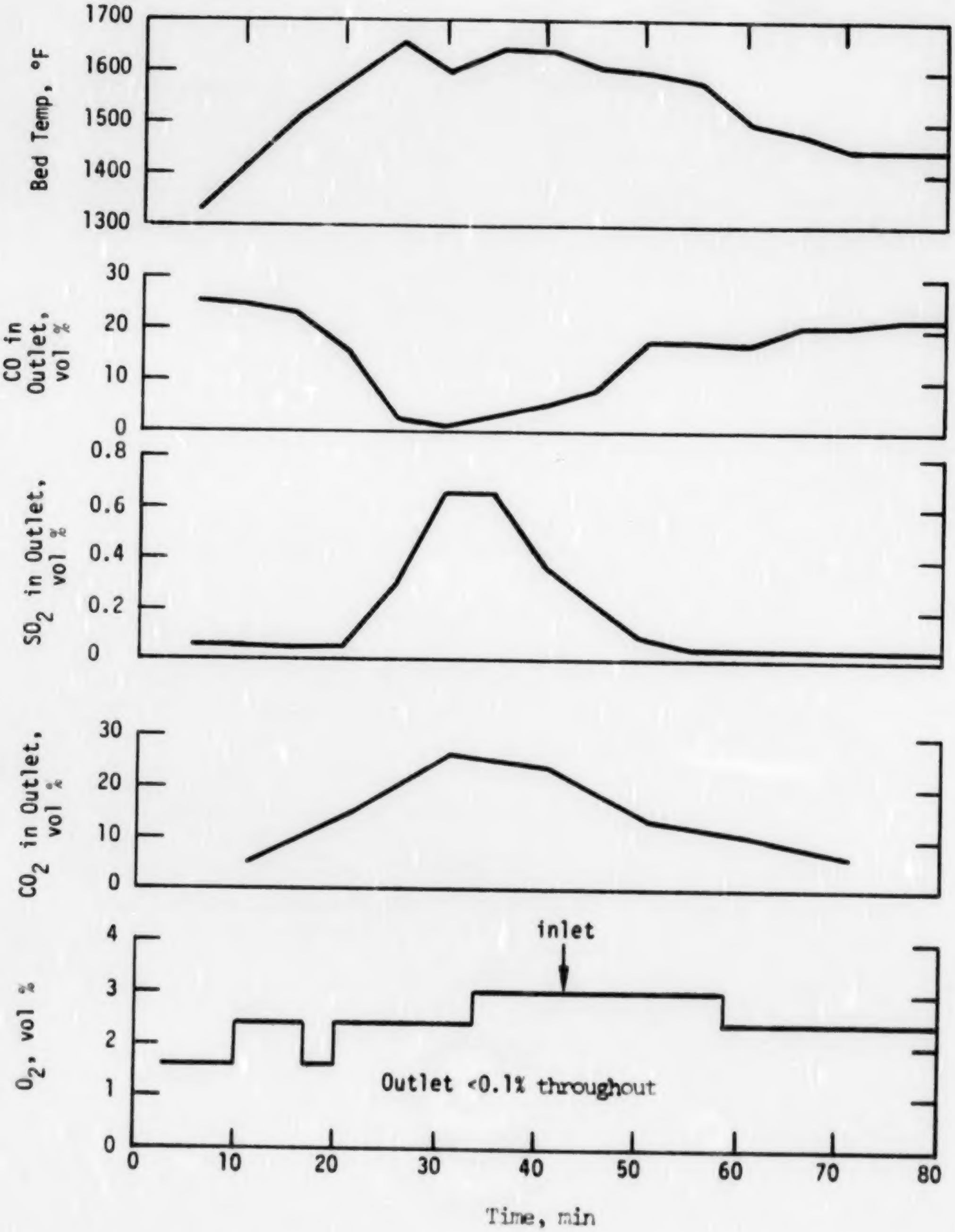


Fig. C-7. Operating Conditions for Experiment CATS-40

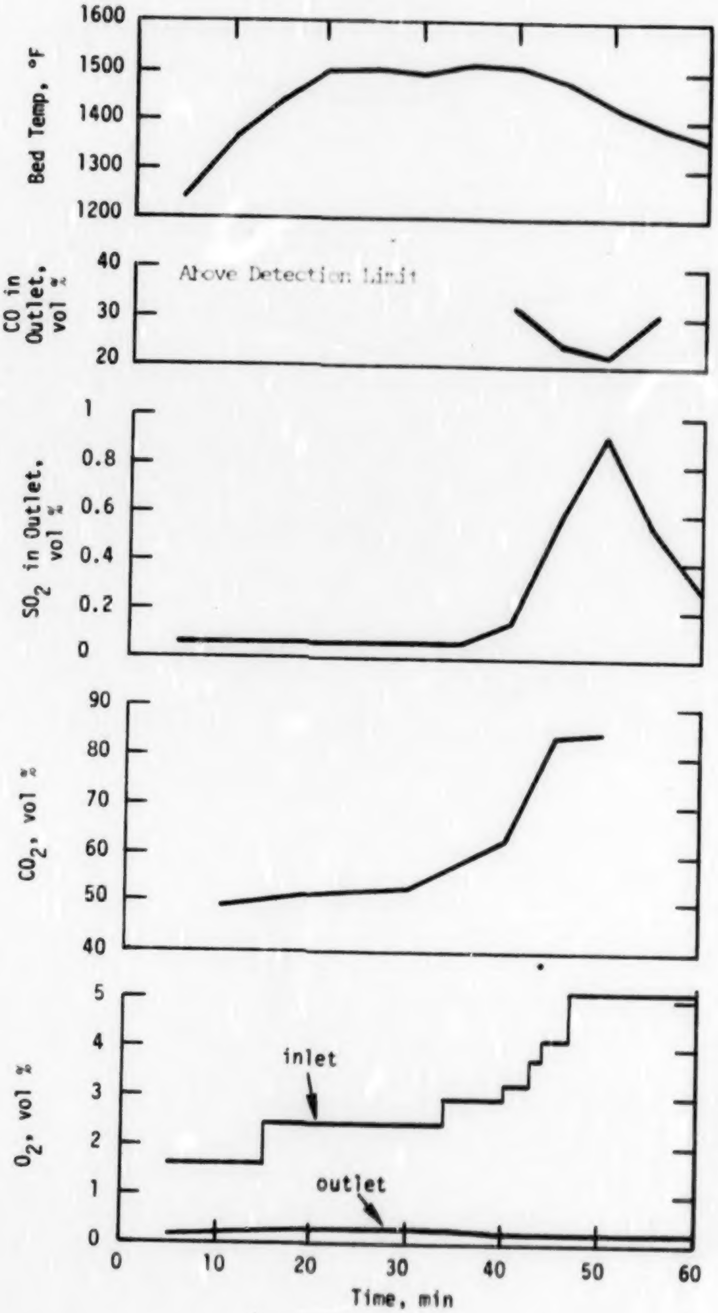


Fig. C-8. Operating Conditions for Experiment CATS-41

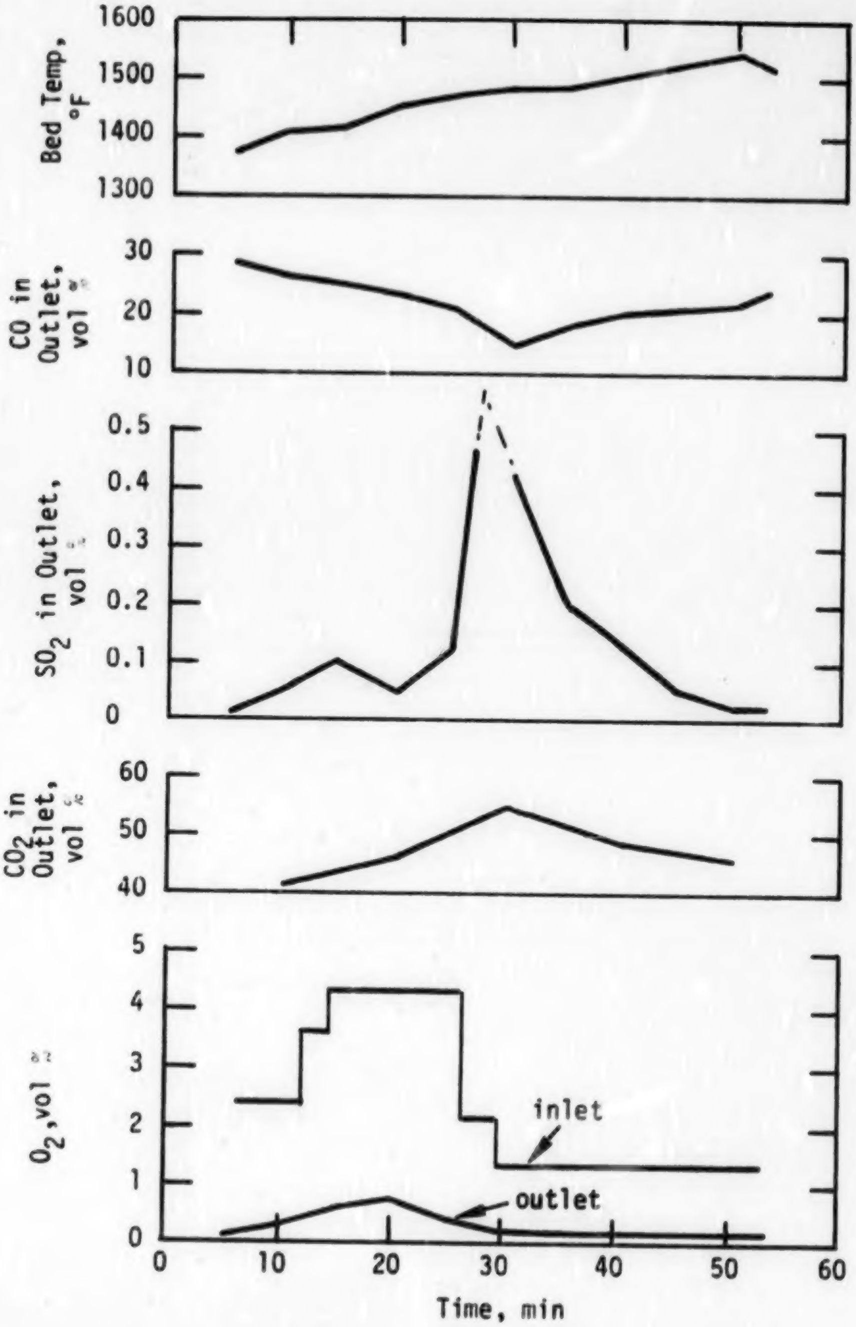


Fig. C-9. Operating Conditions for Experiment CATS-42

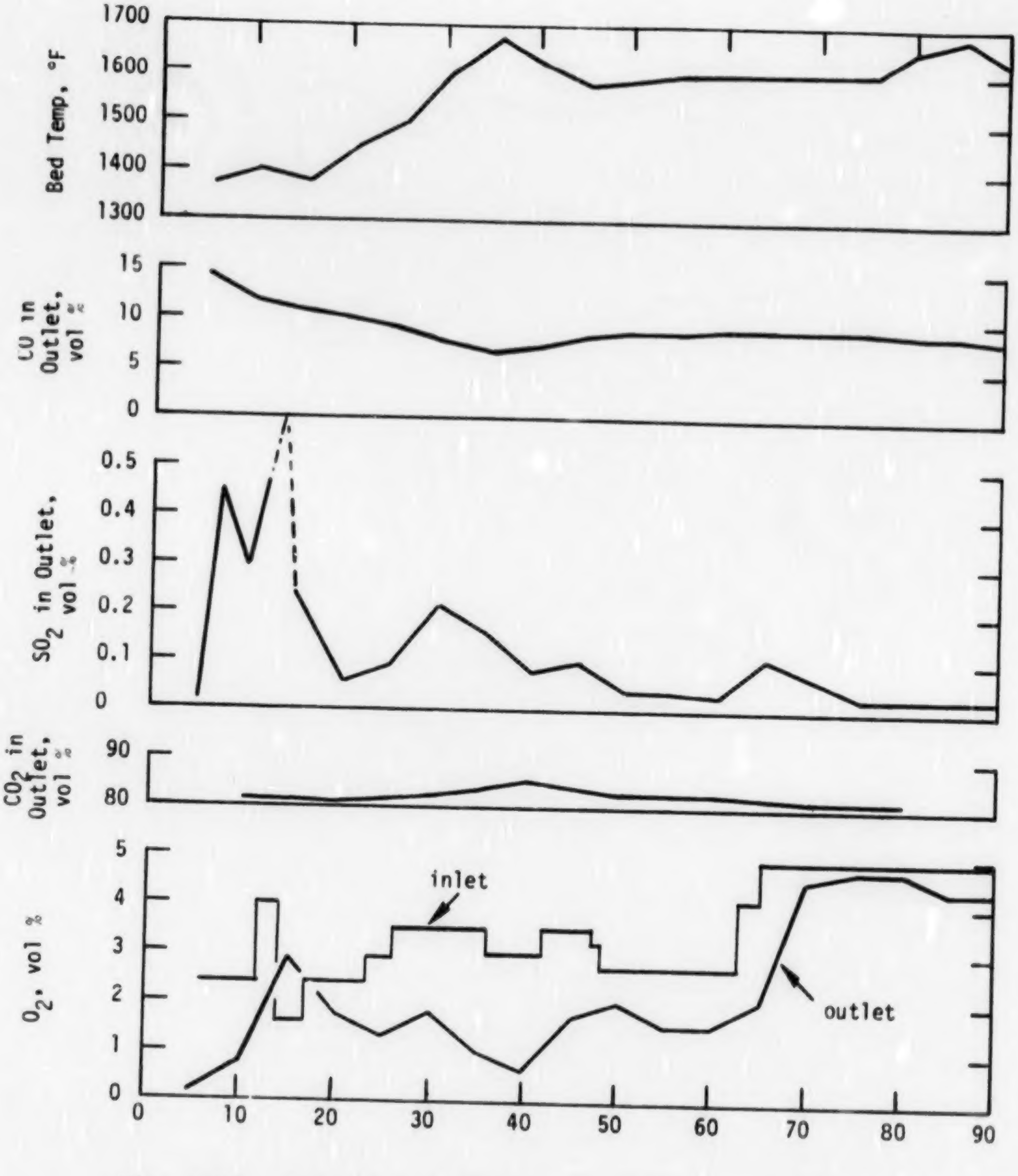


Fig. C-10. Operating Conditions for Experiment CATS-43

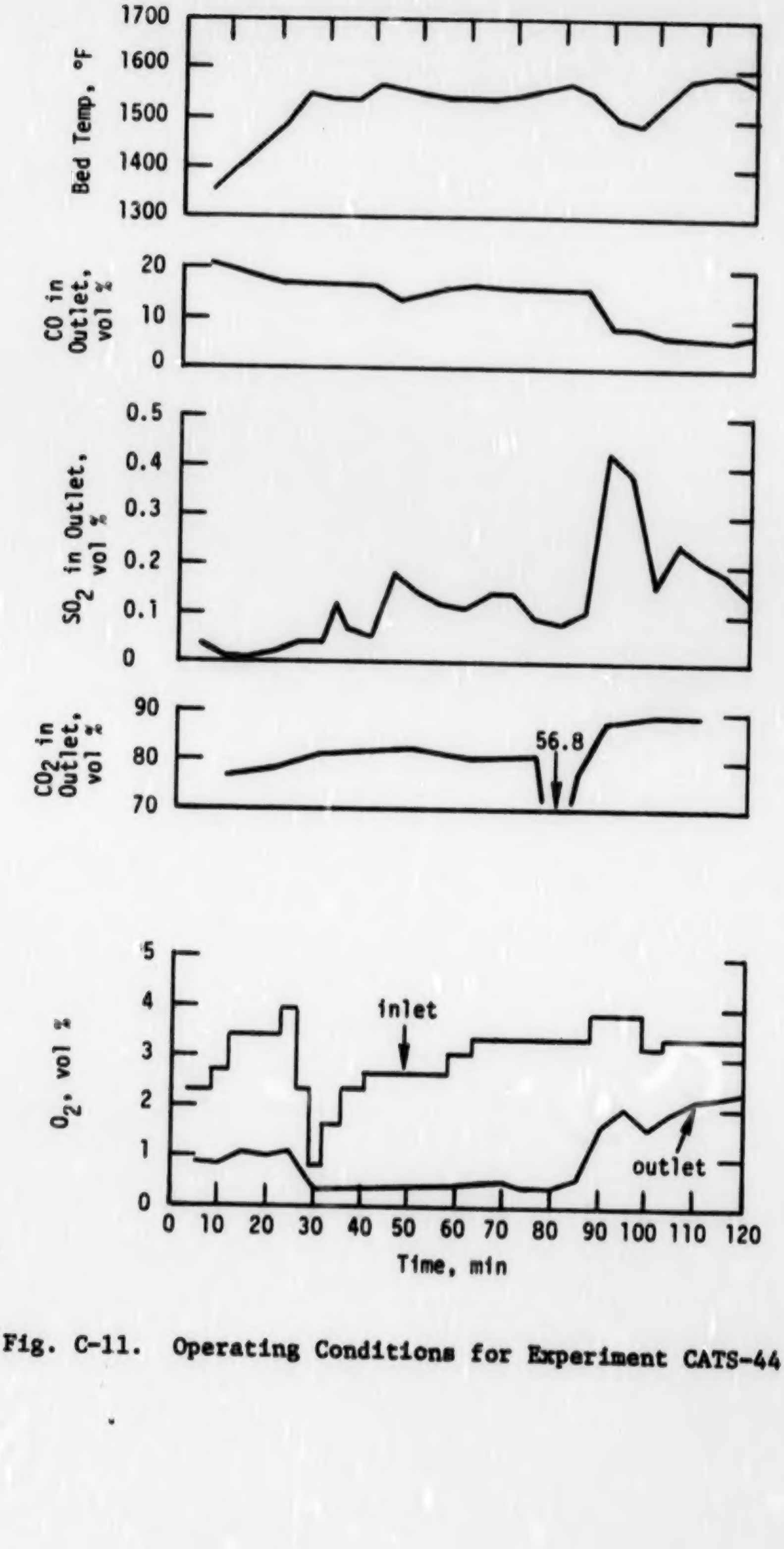


Fig. C-11. Operating Conditions for Experiment CATS-44

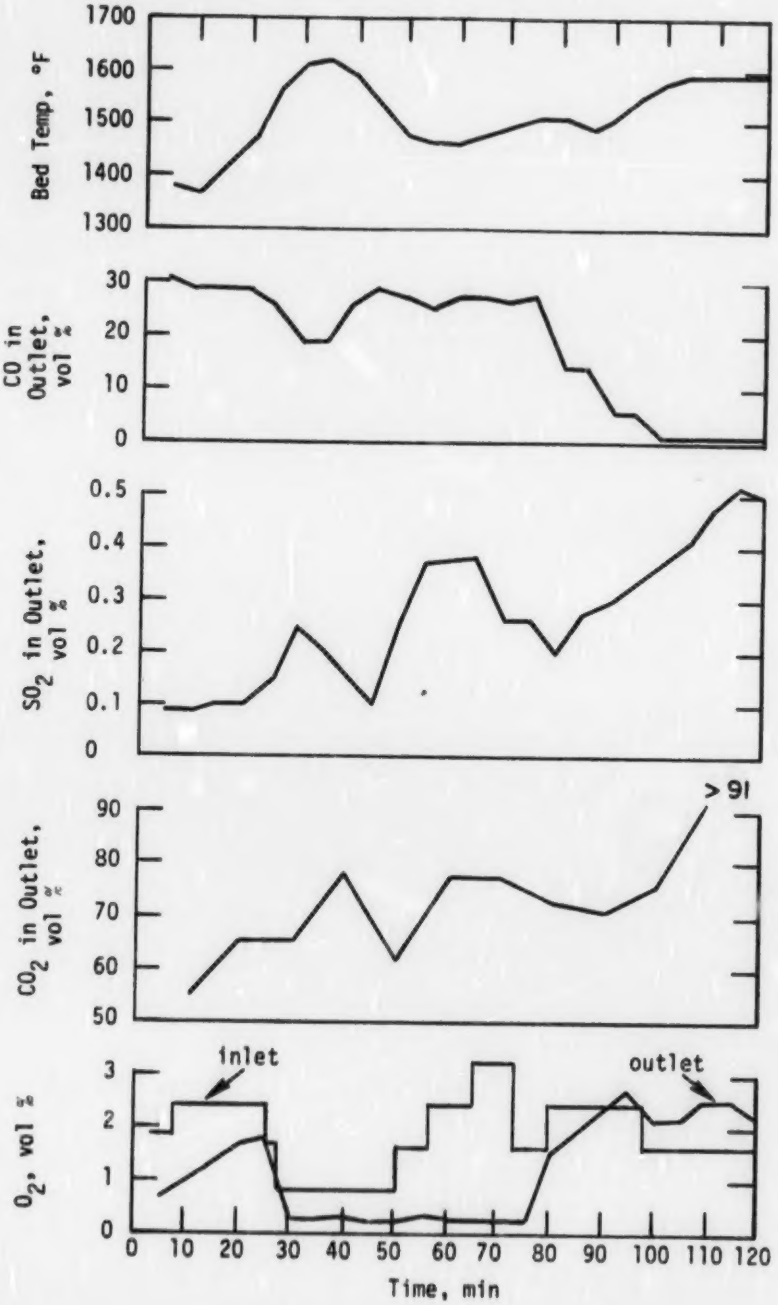


Fig. C-12. Operating Conditions for Experiment CATS-45

Table C-1. Operating Conditions and Results of Experiments CATS-34 to CATS-37

System pressure: 2 atm Superficial gas velocity: 2 ft/sec at 1600°F

Experiment	CATS-34	CATS-35	CATS-36	CATS-37
Operating Conditions				
Reactor	alumina	alumina	SS	SS
Temperature, °F	1210-1670	1220-1620	1200-1620	1175-1460
Reaction time, min	80	80	80	45
Inlet-Gas Flow Rates				
CO, cfm at 70°F, 1 atm	0.09	0.09	0.37	0.37
CO_2, cfm at 70°F, 1 atm	0.07	0.07	0.32	0.32
O_2, cfm at 70°F, 1 atm		0.02-0.04		0.03-0.09
H_2O, cfm at 70°F, 1 atm			0.02	
N_2, cfm at 70°F, 1 atm	0.17	0.14	0.71	0.61
Total	0.33	0.33	1.42	1.36
Bed Data				
Weight of initial bed, g $CaSO_4$ (Drierite)	140	140	570	570
Weight of sulfur in initial bed, g	31.7	31.7	128.8	128.8
Weight of final bed, g	72	77.5	492	473
Concentration of sulfur in final bed, wt %	32	14.8	23.3	21.4
Weight of sulfur in final bed, g	23	11.5	114.5	101.3
Concentration of sulfide in final bed, wt %	20.9	0.02	3.6	2.4
Weight of sulfide in final bed, g	15.1	0.015	17.7	11.5
Final Bed Composition				
CaS, wt %	47.1	0.05	8.1	5.5
$CaSO_4$, wt %	46.6	62.8	83.5	80.8
$CaCO_3$-CaO, wt % (by difference)	6.3	37.2	8.4	13.7
Sulfur Balance				
Weight of sulfur as CaS, g	15.1	0.02	17.7	11.5
Weight of sulfur as $CaSO_4$, g	7.9	11.5	96.7	89.8
Weight of sulfur as SO_2, g	8.9	17.2	1.4	15.7
Weight of sulfur as H_2S, g			4.8	
Total, g	31.9[a]	28.7[a]	120.6[a]	117.0[a]
Percent material balance	100.5	90.5	93.7	91

[a] Does not include weight of sulfur as S_x or COS.

Table C-2. Operating Conditions and Results of Experiments CATS-38 to CATS-41

System pressure: 2 atm Superficial gas velocity: 2 ft/sec at 1600°F

Experiment	CATS-38	CATS-39	CATS-40	CATS-41
Operating Conditions				
Reactor	SS	SS	SS	SS
Temperature, °F	1250-1610	1220-1500	1330-1650	1240-1510
Reaction time, min	80	80	80	60
Inlet-Gas Flow Rates				
CO, cfm at 70°F, 1 atm	0.37	0.1	0.37	0.76
CO_2, cfm at 70°F, 1 atm	0.26	0.5		0.62
O_2, cfm at 70°F, 1 atm	0-0.08	0.02-0.05	0.02-0.04	0.02-0.07
H_2O, cfm at 70°F, 1 atm				
N_2, cfm at 70°F, 1 atm	0.71	0.71	0.97	
Total	1.38	1.34	1.36	1.42
Bed Data				
Weight of initial bed, g $CaSO_4$ (Drierite)	570	570	570	570
Weight of sulfur in initial bed, g	128.8	128.8	128.8	128.8
Weight of final bed, g	450	566	389	432
Concentration of sulfur in final bed, wt %	20.8	22.8	30.6	24.7
Weight of sulfur in final bed, g	93.5	129	119.2	106.8
Concentration of sulfide in final bed, wt %	1.12	0.02	21.7	10.9
Weight of sulfide in final bed, g	5.0	0.1	84.5	47.2
Final Bed Composition				
CaS, wt %	2.5	0.04	49	24.6
$CaSO_4$, wt %	83.5	97.2	38	58.6
$CaCO_3$-CaO, wt % (by difference)	13.9	2.9	13.1	16.9
Sulfur Balance				
Weight of sulfur as CaS, g	5.0	0.1	84.5	47.2
Weight of sulfur as $CaSO_4$, g	88.5	128.9	34.7	59.6
Weight of sulfur as SO_2, g	33.3	3	7.6	8.6
Total, g	126.8[a]	132.0[a]	126.8[a]	115.4[a]
Percent material balance	98.5	102.5	98.5	89.8

[a] Does not include weight of sulfur as S_x or COS.

Table C-3. Operating Conditions and Results of Experiments CATS-42 and CATS-43

System pressure: 2 atm Superficial gas velocity: 2 ft/sec at 1600°F

Experiment	CATS-42	CATS-43
Operating Conditions		
Reactor	SS	SS
Temperature, °F	1370-1540	1370-1680
Reaction time, min	53	90
Inlet-Gas Flow Rates		
CO, cfm at 70°F, 1 atm	0.40	0.14
CO_2, cfm at 70°F, 1 atm	0.49	0.97
O_2, cfm at 70°F, 1 atm	0.02-0.06	0.02-0.07
H_2O, cfm at 70°F, 1 atm		
N_2, cfm at 70°F, 1 atm	0.43	0.14
Total	1.36	1.29
Bed Data		
Weight of initial bed, g $CaSO_4$ (Drierite)	570	570
Weight of sulfur in initial bed, g	128.8	128.8
Weight of final bed, g	507	567
Concentration of sulfur in final bed, wt %	22.2	21.8
Weight of sulfur in final bed, g	112.3	123.4
Concentration of sulfide in final bed, wt %	4.4	0
Weight of sulfide in final bed, g	22.3	0
Final Bed Composition		
CaS, wt %	9.9	0
$CaSO_4$, wt %	75.5	92.5
$CaCO_3$-CaO, wt % (by difference)	14.6	7.5
Sulfur Balance		
Weight of sulfur as CaS, g	22.3	0
Weight of sulfur as $CaSO_4$, g	90.0	123.4
Weight of sulfur as SO_2, g	4.2	6.1
Total, g	116.5[a]	129.5[a]
Percent material balance	90.6	100.5

[a] Does not include weight of sulfur as S_x or COS.

Table C-4. Operating Conditions and Results of Experiment CATS-44

System pressure: 2 atm Superficial gas velocity: 2 ft/sec at 1600°F

Operating Conditions						
Reactor	SS					
Temperature, °F	1350-1590					
Reaction time, min	120					
Time Period, min	0-72	72-82	82-86	86-95	95-99	99-120
Inlet-Gas Flow Rates						
CO, cfm at 70°F, 1 atm	0.28	0.28	0.28	0.14	0.2	0.1
CO_2, cfm at 70°F, 1 atm	1.03	0.69	1.03	1.17	1.17	1.2
O_2, cfm at 70°F, 1 atm	0.01-0.05	0.04	0.04	0.04-0.05	0.04	0.04
H_2O, cfm at 70°F, 1 atm						
N_2, cfm at 70°F, 1 atm		0.34				
Total	1.34	1.35	1.35	1.35	1.41	1.34
Bed Data						
Weight of initial bed, g $CaSO_4$ (Drierite)	570					
Weight of sulfur in initial bed, g	128.8					
Weight of final bed, g	542					
Concentration of sulfur in final bed, wt %	21.3					
Weight of sulfur in final bed, g	115.4					
Concentration of sulfide in final bed, wt %	1.4					
Weight of sulfide in final bed, g	7.6					
Final Bed Composition						
CaS, wt %	3.2					
$CaSO_4$, wt %	84.5					
$CaCO_3$-CaO, wt % (by difference)	12.3					
Sulfur Balance						
Weight of sulfur as CaS, g	7.6					
Weight of sulfur as $CaSO_4$, g	107.8					
Weight of sulfur as SO_2, g	10.3					
Weight of sulfur as H_2S, g						
Total, g	125.7[a]					
Percent material balance	97.6					

[a] Does not include weight of sulfur as S_x or COS.

Table C-5. Operating Conditions and Results of Experiment CATS-45

System pressure: 2 atm Superficial gas velocity: 2 ft/sec at 1600°F

Operating Conditions							
Reactor				SS			
Temperature, °F				1370-1620			
Reaction time, min				120			
Time Period, min	0-35	35-44	44-54	54-79	79-89	89-98	98-120
Inlet-Gas Flow Rates							
CO, cfm at 70°F, 1 atm	0.41	0.41	0.41	0.41	0.17	0.06	0.01
CO_2, cfm at 70°F, 1 atm	0.69	0.93	0.69	0.93	0.93	0.99	1.27
O_2, cfm at 70°F, 1 atm	0.0-0.04	0.04	0.04	0.04	0.04	0.04	0.04
H_2O, cfm at 70°F, 1 atm							
N_2, cfm at 70°F, 1 atm	0.24	—	0.24	—	0.24	0.28	—
Total	1.36	1.38	1.38	1.38	1.38	1.38	1.32
Bed Data							
Weight of initial bed, g $CaSO_4$ (Drierite)				570			
Weight of sulfur in initial bed, g				128.8			
Weight of final bed, g				474			
Concentration of sulfur in final bed, wt %				21.1			
Weight of sulfur in final bed, g				100			
Concentration of sulfide in final bed, wt %				8			
Weight of sulfide in final bed, g				37.9			
Final Bed Composition							
CaS, wt %				18			
$CaSO_4$, wt %				55.7			
$CaCO_3$-CaO, wt % (by difference)				26.4			
Sulfur Balance							
Weight of sulfur as CaS, g				37.9			
Weight of sulfur as $CaSO_4$, g				62.1			
Weight of sulfur as SO_2, g				18.3			
Weight of sulfur as H_2S, g							
Total, g				118.3[a]			
Percent material balance				92			

---

[a] Does not include weight of sulfur as S_x or COS.

APPENDIX D. THERMODYNAMIC CONSIDERATIONS RELATING TO THE CONVERSION OF CALCIUM SULFATE TO CALCIUM CARBONATE

Thermodynamic Considerations Relating to the Conversion of Calcium Sulfate to Calcium Carbonate

The present process being considered for the conversion of $CaSO_4$ to $CaCO_3$ involves a two-step process in which $CaSO_4$ is converted to CaS and CaS in turn is converted to $CaCO_3$. We have attempted to reexamine the thermodynamics of these processes and suggest possible alternative schemes to accomplish conversion of $CaSO_4$ to $CaCO_3$.

Among the many possible reactions arising in the presence of $CaSO_4$, H_2, CO_2, H_2O, CaS, $CaCO_3$, H_2S, predominant ones are:

$$CaSO_4 + 4\ H_2 \rightarrow CaS + 4\ H_2O \tag{1}$$

$$CaS + H_2O + CO_2 \rightarrow CaCO_3 + H_2S \tag{2}$$

$$CaSO_4 + 4\ H_2 + CO_2 \rightarrow CaCO_3 + 3\ H_2O + H_2S \tag{3}$$

$$H_2O + CO \rightarrow CO_2 + H_2 \tag{4}$$

$$CaSO_4 + 4\ CO \rightarrow CaS + 4\ CO_2 \tag{5}$$

$$CaSO_4 + 3\ H_2 + CO \rightarrow CaCO_3 + H_2S + 2\ H_2O \tag{6}$$

$$CaSO_4 + CO \rightarrow CaCO_3 + SO_2 \tag{7}$$

$$SO_2 + 3\ H_2 \rightarrow H_2S + 2\ H_2O \tag{8}$$

The equilibrium constants for these reactions at selected temperatures are tabulated in Table D-1.

In the presence of $CaSO_4$, H_2, and CO_2, reaction (1) may proceed to a much greater extent than reaction (3). However, when $PH_2O/PH_2 \geq \sqrt[4]{K_1}$, where K_1 is the equilibrium constant for reaction (1), reaction (1) is suppressed and reaction (3) proceeds.

Thermodynamic considerations of these and relevant reactions follow:

Table D-1. Equilibrium Constants for Predominant Reactions in the Conversion of Calcium Sulfate to Calcium Carbonate at Selected Temperatures

	Reactions	Temperature					
		1000°F		1200°F		1400°F	
		ln K	K	ln K	K	ln K	K
(1)	$CaSO_4 + 4H_2 \rightarrow$ $CaS + 4H_2O$	21.768	2.818×10^9	21.025	1.352×10^9	20.329	6.74×10^8
(2)	$CaS + H_2O + CO_2 \rightarrow$ $CaCO_3 + H_2S$	-1.862	0.153	-3.759	0.023	-5.199	5.52×10^{-3}
(3)	$CaSO_4 + 4H_2 + CO_2 \rightarrow$ $CaCO_3 + 3H_2O + H_2S$	19.896	4.37×10^8	17.265	3.148×10^7	15.129	3.719×10^6
(4)	$H_2O + CO \rightarrow$ $CO_2 + H_2$	1.373	3.949	0.710	2.033	0.235	1.265
(5)	$CaSO_4 + 4CO \rightarrow$ $CaS + 4CO_2$	27.25	6.853×10^{11}	23.863	2.31×10^{10}	21.268	1.724×10^9
(6)	$CaSO_4 + 3H_2 + CO \rightarrow$ $CaCO_3 + H_2S + 2H_2O$	21.269	1.728×10^9	17.976	6.407×10^7	15.364	4.704×10^6
(7)	$CaSO_4 + CO \rightarrow$ $CaCO_3 + SO_2$	-1.442	0.236	-0.787	0.455	-0.270	0.763
(8)	$SO_2 + 3H_2 \rightarrow$ $H_2S + 2H_2O$	22.713	7.316×10^{10}	18.763	1.408×10^8	15.634	6.164×10^6

(a) At 1000°F from reaction (1) and (3)

$$\frac{(PH_2O)^4}{(PH_2)^4} \approx 2.82 \times 10^9 \rightarrow PH_2O/PH_2 \approx 230$$

$$\frac{(PH_2O)^3\ (PH_2S)}{(PH_2)^4(PCO_2)} \approx 4.37 \times 10^8$$

Let $PH_2O/PH_2 > 230$, reaction (1) does not substantially proceed and the following equilibrium condition holds for (3):

$$\frac{PH_2S}{(PH_2)(PCO_2)} < 36$$

For reaction (4),

$$\frac{(PCO_2)(PH_2)}{(PH_2O)(PCO)} \approx 3.95 \text{ or } \frac{PCO_2}{PCO} > 909$$

For reaction (5) to reach equilibrium,

$$\frac{(PCO_2)^4}{(PCO)^4} \approx 6.85 \times 10^{11} \text{ or } \frac{PCO_2}{PCO} \approx 910$$

Therefore, the amount of CO produced by reaction (4) is just enough to initiate reaction (5). To prevent this, PH_2O/PH_2 should be greater than 230. Reaction (6) would be in equilibrium when (3) and (4) are in equilibrium.

If the feed gas contains: 0.04 atm H_2, 9.8 atm H_2O, 0.2 atm CO_2.

$$PH_2O/PH_2 = 245$$

$$\frac{PH_2S}{(PH_2)\ (PCO_2)} \approx 30$$

Equilibrium PH_2S = 0.28 atm
Stoichiometric PH_2S = 0.01 atm [from (4)]

Therefore, total consumption of H_2 is expected.

By making PH_2O/PH_2 high enough, reaction (3) would be predominant. Similar calculations for T = 1400°F indicate that the actual equilibrium constant, $PH_2S/(PH_2)\ (PCO_2)$, at lower temperature is much greater than at higher temperature. Thus, lower temperature is preferrable. The PH_2O/PH_2 ratio should not be made too great because the actual equilibrium constant, $PH_2S/(PH_2)(PCO_2)$, is proportional to $[1/(PH_2O/PH_2)^3]$. At too low a temperature,PH_2 is very low and the partial pressure of H_2S will be correspondingly low.

It is recognized that the above reaction produces H_2S at partial pressures too low to permit subsequent sulfur recovery reactions. Nevertheless, it is recommended that the conditions described as being favorable for reaction (3) be experimentally verified. The results of such an experiment can be expected to provide greater insight into the problems.